THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

INTEGRATED STUDIES

FACTORS CONTRIBUTING TO THE STRENGTH PROPERTIES OF A SHEET OF PAPER - I

Project 1513

Progress Report Sixteen

to

PULP EVALUATION GROUP

February 25, 1957

TABLE OF CONTENTS

PHOTOMICROGRAPHS

I. SUMMARY

The ultimate objective of the Project 1513 integrated studies is the complete evaluation of the factors contributing to the strength of a sheet of paper. On the basis of what is known from the literature and what has been studied under this project so far, these factors may be cataloged with some assurance. They are: the inherent fiber strength, the inherent bonding strength, the external specific surface of the unbeaten fiber, factors of fiber flexibility and conformability, factors relating to swollen specific volume, fiber length and fiber length distribution, and the bonding substance released on beating.

Furthermore, it can be stated on the basis of work done to date how some of these factors arise quantitatively and how some of them affect strength properties. Enough is known about others to permit qualitative estimates of their effects.

It was the object of the particular work reported here to evaluate some of the factors producing strength and to place the others in such perspective as to permit proper orientation of the future work. These results are summarized under four main headings.

THE SURFACES OF PULP FIBERS

Experimental comparison of various methods of surface area determination has shown that the geometric, silvering, and filtration resistance methods agree exceptionally well on the absolute value of the external specific surface of unbeaten fines-free pulp. However, only the filtration resistance method satisfactorily accounts for the large surface area contribution in the fines fraction in beaten pulp. The regular increase in both external and internal surface with time of

beating and the energy consumption involved indicates that beating is comparable to the common size reduction processes following Rittinger's Law.

STRENGTH PROPERTIES--GENERAL CONSIDERATIONS

The strength data for handsheets prepared from unclassified (whole) pulp and from classified (fines removed) pulp show that the fines fraction has but little effect on burst and tensile strength of paper from ball mill beaten pulp but does contribute greatly to the velocity-viscosity product and fold strength of paper. The presumed importance to strength of a "cementing substance," revealed photomicrographically, is discussed.

The basic weakness of the freeness test for prediction of pulp strength is again established as its oversensitivity to fines. The possible utility of apparent density as a strength prediction variable is outlined.

BONDED AREA

By correlating tensile strength with the bonded area indicated from specific scattering coefficient data, it appears that the total dry area available for fiber bonding, which is effective in developing tensile strength, remains constant with refining time. This available area is unaffected by production of fines or the degree of fibrillation. An improved and simplified method for obtaining more reliable estimates of relative bonded area is presented.

FIBER SWELLING

It is shown from the experimental data that wet fiber specific volume is directly related to the ultimate amount of fiber-to-fiber bonding in paper. Water-swollen beaten fibers are in a more flexible state than unbeaten fibers and, when wet-pressed, are in more intimate contact and thus have more potential bonding area. Fibrillation, while not directly connected with bonding through surface area development, contributes to more intimate contact of the plasticized fibers through the effect of surface tension forces drawing the fibers closer together during drying.

Filtration resistance measurements of wet fiber specific volume show no difference between classified and unclassified pulps of the same beater interval. The wet fiber specific volume obtained by the centrifuge method on classified pulps is very close to that determined by filtration resistance. The utility of the simple centrifuge test in pulp strength prediction may thus be justified.

In general discussion, the unevaluated topics of fiber length distribution, inherent bonding strength and others are listed for intensive study in the course of a comparison of strength properties of different pulps. Also suggested for future work is a quantitative study of the contribution of different beating engines to the different factors of pulp strength now delineated. Knowledge gained through the first phase of the integrated studies provides a better means of measuring and interpreting significant properties in the comparison of pulps at various degrees of refining.

II. A UNIFIED APPROACH TO PULP EVALUATION

One approach in the attack of a complex problem which is too large to solve all at once is to break it down for manipulation into convenient parts. Contrariwise, common wisdom tells us that exclusive attention to such an approach will make it impossible for us to visualize the whole problem--"He can't see the woods for the trees."

Because of the bewildering complexity of the relationships involved in the formation of that common material, a sheet of paper, the "fragmentary" approach to such problems as pulp strength prediction has been the rule. The conscientious and well-informed workers who delved into such topics as "the relation between beating degree and the bursting strength of paper" were not deliberately ignoring the "woods" of the larger problem of pulp strength. But the proliferation of investigations such as these led many technical men into the predicament of the legendary blind men who could not agree on the description of an elephant. The air was rent with polemics--"Sound and fury, signifying nothing," undigested information accumulated at an ever-increasing rate, but understanding did not increase!

As this situation became acute, many thoughtful technical men in the paper field called for a comprehensive over-all survey of the problems of pulp evaluation, so that true understanding could be advanced.

It was with this long view that a number of the members of the Institute formed the Pulp Evaluation Group. It was to implement this view that the staff advisory committee of Project 1513 recommended, and the Technical Committee adopted, a plan for so-called "integrated studies" of "Factors Contributing to the Strength Properties of a Sheet of Paper." Here was a plan whereby the jigsaw pieces of the "fragmentary" approach were to be put together; here was an approach wherein the experimenter was charged with gaining familiarity with each of a myriad of individual details and then backing off to take the long view.

In these days of high-speed computers, many such problems are treated by what may be called the "massive statistical attack." Reams of data are accumulated, coded, and fed into the capacious maw of a "Univac" which rapidly and accommodatingly grinds out information on reactions and interactions of virtually infinite order. While such an approach may conceivably have some validity in a later portion of these studies, it was apparent that a careful scrutiny of the various <u>means</u> of obtaining data was an essential part of the integrated studies. Therefore, the indicated approach was to gather, not a massive <u>amount</u>, but a selected <u>variety</u> of evaluation data of various kinds and then to interrelate these data by logical means.

In approaching this problem, the participating staff members have kept in mind that incidental short-range gains and empirical discoveries can be of value to the membership and should not be ignored in the quest of unified concepts. Thus, the preceding reports in this series, as well as the present one, include details of techniques for evaluation of particular pulp properties and also include observations as to possibly important empirical correlations which may be of use in process control.

In the main, however, emphasis on the 1513 integrated studies has been the development of a theoretically sound, unified concept of the problem of pulp evaluation. The major goal has been the discovery of what pieces (evaluation tools and individual fundamental phenomena) belong in the puzzle and how they fit.

The staff investigators believe that much has been accomplished in the direction of that goal; the sections which follow are devoted to a detailed analysis of that progress achieved in the first phase of the integrated studies. Areas of uncertainty are still large, so that within the pages to follow, some diversity of view is yet apparent. The over-all plan of this report has been to take a long view from several different vantage points and to indicate where our present knowledge permits unity of thought and where more information is needed.

Specifically, the organization of this report is as follows: The brief Procedure section is followed by four discussion sections representing four vantage points on the general problem: External and Internal Surfaces of Fibers, Sheet Strength Properties in General, Bonded Area, and Fiber Swelling. These specific sections are followed by a general discussion section where unifying concepts are developed. A discussion of some of the important items of experimental information required in the realization of the ultimate objective constitutes the closing section. This is the first phase of the integrated studies and represents, it is believed, a beginning toward understanding how the factors under consideration are of value as a basis for predicting the strength properties of a sheet of paper.

III. EXPERIMENTAL PROCEDURES

This initial phase of the integrated studies concerned some of the variables which affect fiber bonding such as fiber surface areas, bonded area, and specific volume. The details concerning the individual measurements per se have been reported in Progress Reports 13-15 covering the following subjects:

Progress Report Number	Subject Integrated Studies of Surface Properties of Wood Pulp
13	Effect of Beating on Filtration Resistance and its Components of Specific Surface, Specific Volume, and Compressibility
14	Influence of Beating on the Total Surface Area and Pore-Size Distribution of Sulfite Pulp--Nitrogen Gas Adsorption Technique
15	Revision and Study of Dye Adsorption Procedure for Estimation of the External Specific Surface of Wood Pulp

This report, number 16, treats the above studies as a whole and attempts to correlate the properties measured in the previous studies with handsheet physical properties. All the measurements in Progress Reports 13-16 have been made on the same pulp samples to provide a common basis for comparison. A bleached softwood pulp was selected and refined in a ball mill for minimum fiber cutting and maximum reproducibility. At each of seven beating intervals, some of the pulp was used to form handsheets which were subsequently dried and used for the evaluation of physical properties. The remaining pulp was formed into handsheets (to allow for the same loss of fines) and then stored in a wet condition for measurement of pulp properties.

Recognizing the important effect of fines on pulp surface properties, a second set of samples was formed from the same beating intervals in a similar manner, but in addition, the pulps were fractionated to remove fines. Thus, two sets of pulp samples and handsheets were available for testing, each at the same beating intervals: (1) unclassified whole pulp and handsheet pulp, and (2) classified whole pulp and handsheet pulp.

The raw material used for the integrated studies was a bleached sulfite pulp taken from the third press of a pulp drier at the Weyerhaeuser Timber Company, Pulp Division, Longview mill. The pulp was shipped to the Institute as a wet lap of roughly 43% moisture content in barrels lined with wax paper. Microscopic analysis showed it to be composed of the following wood species: 85-90% hemlock, 10-20% fir, and a small amount of larch. The pulp was shredded in a laboratory pulp breaker and stored in polyethylene bags at 5°C. until required for experimentation. No preservative was added initially, but 1% formalin solution (on the wet pulp basis) was added to the pulp at a later date as a precaution to forestall bacterial attack during the long storage period.

The strength properties of this pulp were studied by beating the pulp in a ball mill and evaluating the changes in chemical and physical properties of handsheets prepared from the beaten stock. The ball mill was chosen in preference to the Valley beater or other refining devices as it minimizes fiber cutting. The action is primarily that of maceration or "wet beating," eliminating for the most part the effects of changing fiber length distribution on handsheet properties and thus simplifying the problem of characterizing the changes produced in the sheets. The ball mill, although it develops strength in pulp slowly, is a very reproducible beating device. Special care was taken in charging the mill and in its operation to insure maximum reproducibility. The details of this procedure are given in Appendix A-1. Details of the preparation of the classified pulps and handsheets used in studying the effect of fines on sheet properties are given in Appendix A-2.

Handsheets were made from the beaten pulp at various beating intervals according to Institute Method 411 and discussed in detail in Appendix A-3. The sheets were conditioned under standard conditions (50% R.H. and 73°F.) and physical properties evaluated on these conditioned sheets. To insure maximum precision and accuracy, handsheets were weighed individually for basis weight control, and ten instead of the usual five test sheets used for the physical property evaluation. Standard Institute methods were used for the physical and chemical characterizations of the handsheets wherever possible, but a variety of special tests necessary for a more complete study of the extent of bonding, fiber strength, and other important properties were also determined. Some of these tests measure rather complex functions of pulp properties and sheet properties and are therefore described in the appropriate section of the report with the analysis of the data obtained by these tests.

The following table summarizes the physical and chemical tests that were used to characterize the pulp and handsheets prepared from these pulps. (Where standard tests were used, they are indicated by the Institute test number; nonstandard tests are itemized briefly at the bottom of the table.)

TABLE I

PHYSICAL AND CHEMICAL TESTS

	Institute Method
Conditioning	503
Basis weight (individual sheets)	504
Caliper (5 sheets simultaneously)	508
Apparent density	508
Bursting strength	510
Tearing strength	512
Gurley air porosity	514
M.I.T. fold	Part II, 513
Clark rigidity and rigidity factor	536
Alpha-cellulose	421
Ash	422
Extractives	11

Soluble lignin: Appendix A-4
Cupriethylenediamine viscosity: Appendix A-4
External surface of pulp - silvering: (3, 4)
Load-elongation: Baldwin-Southwark tester
Zero-span tensile: Baldwin-Southwark tester (IPC jaws)
Thwing formation number
VVP (IPC viscosity-velocity product): Appendix A-5
Scattering coefficient: Section VI-C
Microscopic measurements: Appendix A-6

The summarized experimental data are given in Appendix B: pulp properties, Appendix B-1; handsheet properties, Appendix B-2; fiber dimensions, Appendix B-3.

IV. THE EXTERNAL AND INTERNAL SURFACES OF WOOD PULP FIBERS

A. SUMMARY

This first discussion section of the integrated studies report is devoted to a comparison and evaluation of methods of surface area measurement. It is shown that the geometric, silvering, and filtration resistance methods agree exceptionally well on the absolute value of external specific surface of unbeaten, fines-free pulp. It is shown that the filtration resistance and dye adsorption methods agree quite well on the increase in surface area upon beating of pulp, after removal of fines. The silvering and dye adsorption methods agree on the surface area of beaten pulp with no fines removal. Only the filtration resistance method satisfactorily accounts for the large surface area contribution of the fines fraction in beaten pulp.

A comparison of energy requirements for production of increased external and internal surfaces of pulp in the ball mill shows that such process is equivalent to the common size reduction operations. The regular increase in both external and internal surface with time indicates that Rittinger's Law for size reduction holds for the beating of pulp.

In the latter part of this section may be found a discussion of technical applications of surface area measurements to paper mill problems. The limitations of the methods and the particular situations in which they may be of use are examined in detail.

B. INTRODUCTION

In the consideration of factors affecting the strength of a sheet of paper, there need be no question, "Why study fiber surfaces?" It is self-evident that the nature and extent of the surfaces of the fibers which make up a sheet have a profound effect on the properties of the sheet. The better we understand the surfaces of cellulose fibers, the better products we can produce therefrom.

There are many surfaces to be considered in analyzing a fiber. Not only is there the external surface of the primary wall, etc., but there are the surfaces of the pits and the surface of the lumen to consider. "The specific external surface" (surface area per gram of fiber) is not a specific, immutable property of a given fiber, but is something different for each type of measurement and varies markedly with the degree of swelling of the pulp. Also there exists, in addition to these microscopically visible surfaces, a much larger "internal surface" accessible to water molecules--and to molecules of gas in the case of dry pulps prepared by solvent exchange.

In the literature are many methods for the determination, or at least the estimation, of the surface of cellulose fibers. No direct comparison of more than three of these methods has been made at any one time. Considering that the techniques for all such methods have been improved greatly in the past few years, it was felt most desirable that an extensive comparison of all methods of current interest be made as a key portion of the integrated studies.

In brief review, the methods and their backgrounds are described below:

1. Geometric Method. The specific external surface of unbeaten fibers may be quite accurately, if tediously, determined by measurement of the perimeter of cross sections of a representative fiber population. In this study, the method of Graff, Schlosser, and Nihlen (1) was employed. In carrying out the work, improved methods for the determination of population count were used.

2. Silvering Technique. The decomposition of hydrogen peroxide solution is catalyzed by a thin layer of silver deposited on the fibers, in the technique devised by James d'A. Clark (2). Modifications in the method developed by Browning and Baker (3) and Browning (4) were used for this study.

3. Filtration Resistance. By use of appropriate computational techniques, the resistance to fluid flow through a bed of packed fibers may be related to the surface area of these fibers at the hydrodynamic plane of shear. This method was employed for fixed beds by Sullivan and Hertel (5) and Fowler and Hertel (6) and brought to a high degree of accuracy by Robertson and Mason (7). Ingmanson (8), however, demonstrated advantages of employing a dynamic bed. For the purposes of this study, further improvements and refinements in the constant-rate filtration method were made, as described in Progress Report Thirteen (9).

4. Dye Adsorption. Estimation of the surface of cellulose fibers from the amount of sparingly soluble material adsorbed has been proposed by Hess and Gramberg (10), Stamm and Millett (11), and Beamesderfer, Thode, Chase, and Hubbard (12). The technique of the latter workers, employing the dyestuff, Benzo Fast Scarlet 4BSA (C. I. 327), was completely revised for the purposes of the integrated studies and reported in

Progress Report Fifteen (13).

5. Gas Adsorption. Many investigators such as Grace and Maass (14), Emmett and De Witt (15), Assaf, Haas and Purves (16), and Hunt, Blaine, and Rowan (17) have used the adsorption of nitrogen gas on solvent-dried fiber to determine internal surfaces of cellulose fibers. Recently, Haselton (18, 19) and Merchant (20) have contributed a great deal to our knowledge of what occurs during gas adsorption and during the associated solvent-drying operation. In Progress Report Fourteen (21), a description is given of the latest gas adsorption procedures employed for the present investigation.

C. COMPARISON OF SURFACE AREA DETERMINATIONS

First, it is of interest to note the very close correspondence of values obtained for unbeaten, classified pulp by all three of the independent methods for external surface measurement. Table II shows the values of external specific surface rounded off to the nearest 100 sq. cm./gram on the unbeaten fines-free pulp.

TABLE II

EXTERNAL SPECIFIC SURFACE OF CLASSIFIED UNBEATEN PULP

Method	External Specific Surface, sq. cm./g.	Reference
Geometric	7,400	Appendix C-2
Silvering	7,600	Table I, Progress Report Fifteen
Filtration Resistance	7,600	Table IV, Progress Report Thirteen
Dye adsorption[1]	7,400	Table I, Progress Report Fifteen

[1] Arbitrary calibration makes this figure partly dependent on silvering results.

Since the fibers used in the geometric study were prepared by a solvent displacement technique, they are essentially unshrunken.* It is thus most encouraging to find such close agreement with the filtration resistance method. The validity of the computational scheme employed in the latter method is confirmed by these observations.

A glance at the data for external specific surface area as a function of beating time for the three methods of filtration, dye adsorption, and silvering, and for both classified and unclassified pulps shows an amazing correspondence for four of the six curves (Figures 1-3). The classified-filtration, unclassified-dye adsorption, classified-dye adsorption, and the unclassified-silvering curves appear very nearly identical (see Figure 4). To be sure, the classified filtration curve is closest to a straight line, while the others show a slight tendency to "droop" at the highest beating intervals, but all four could be regarded as essentially a single curve. Not too deep a meaning should be read into this apparent fine agreement of the three diverse methods. The external surface area of beaten pulp fibers is still not known--however, we can say with some certainty more than was previously realized:

1. The dye adsorption and the silvering methods apparently determine equivalent aspects of the external surface of whole pulp. It is obviously not the same surface, else the classified silvering values would not be so divergent.

2. The dye adsorption and silvering methods determine some aspects of the surface of whole pulps equivalent to the

* For the benefit of the reader interested in this method, it should be pointed out that a typographical error in the original paper by Graff et al. plus an error in abstracting that paper have led later workers to believe that the geometric method gives spuriously low values. Actually, such was never the case. A sulfite pulp, for example, in Graff's original paper actually had an indicated area of 8000 cm.^{2}/g. if properly computed from his data.

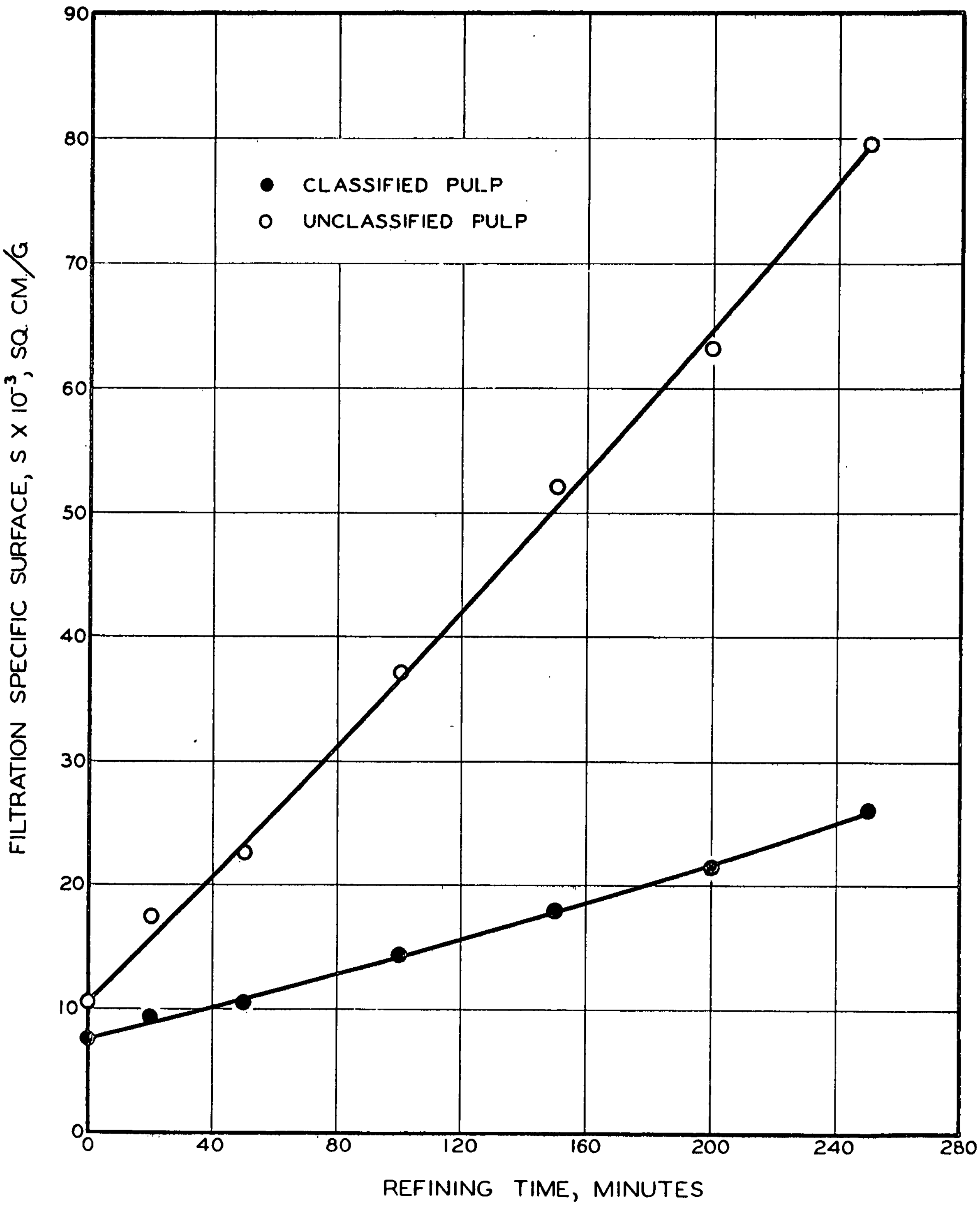

Figure 1

Filtration Specific Surface as a Function of Refining Time

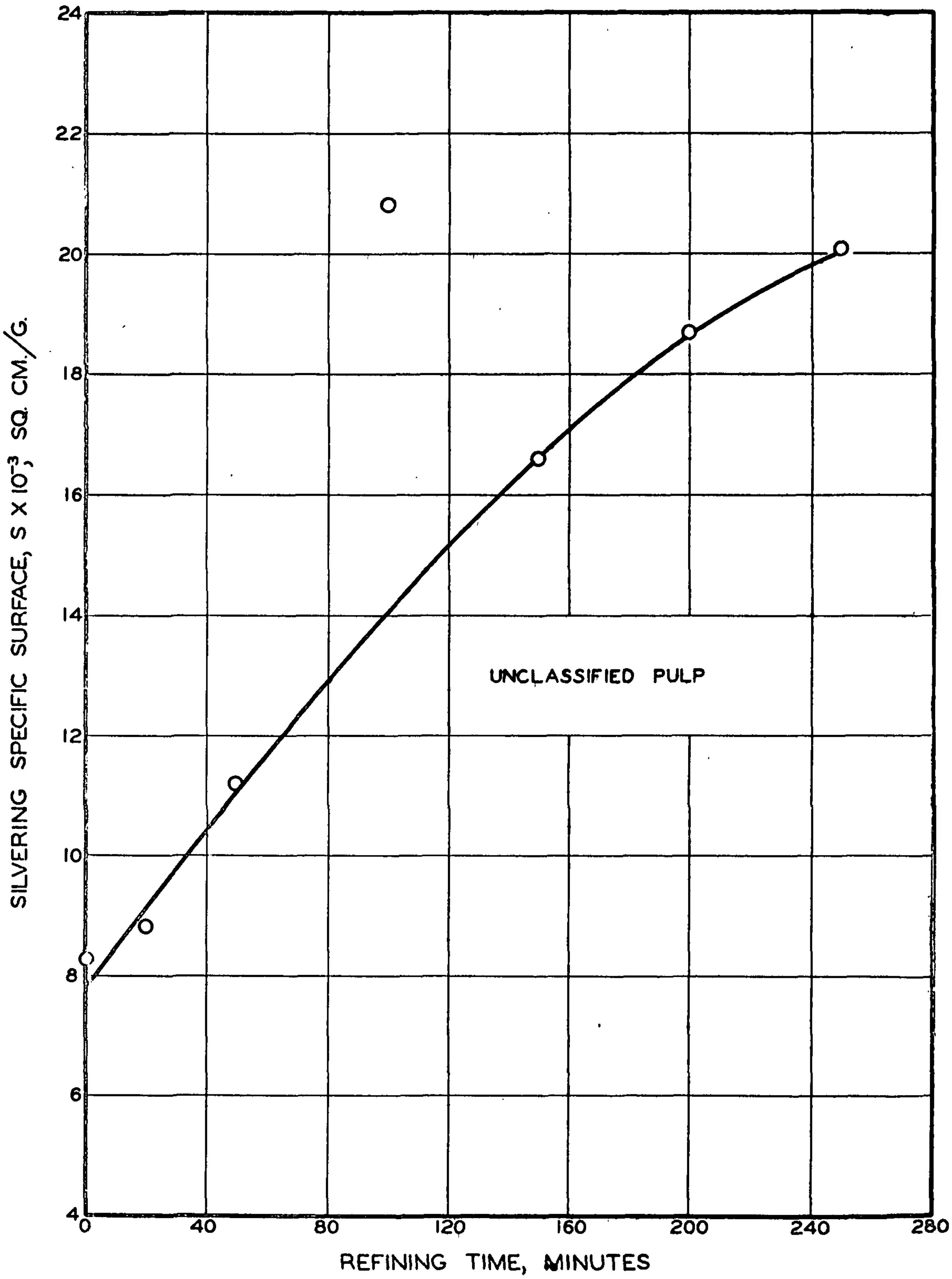

Figure 2

Silvering Specific Surface as a Function of Refining Time

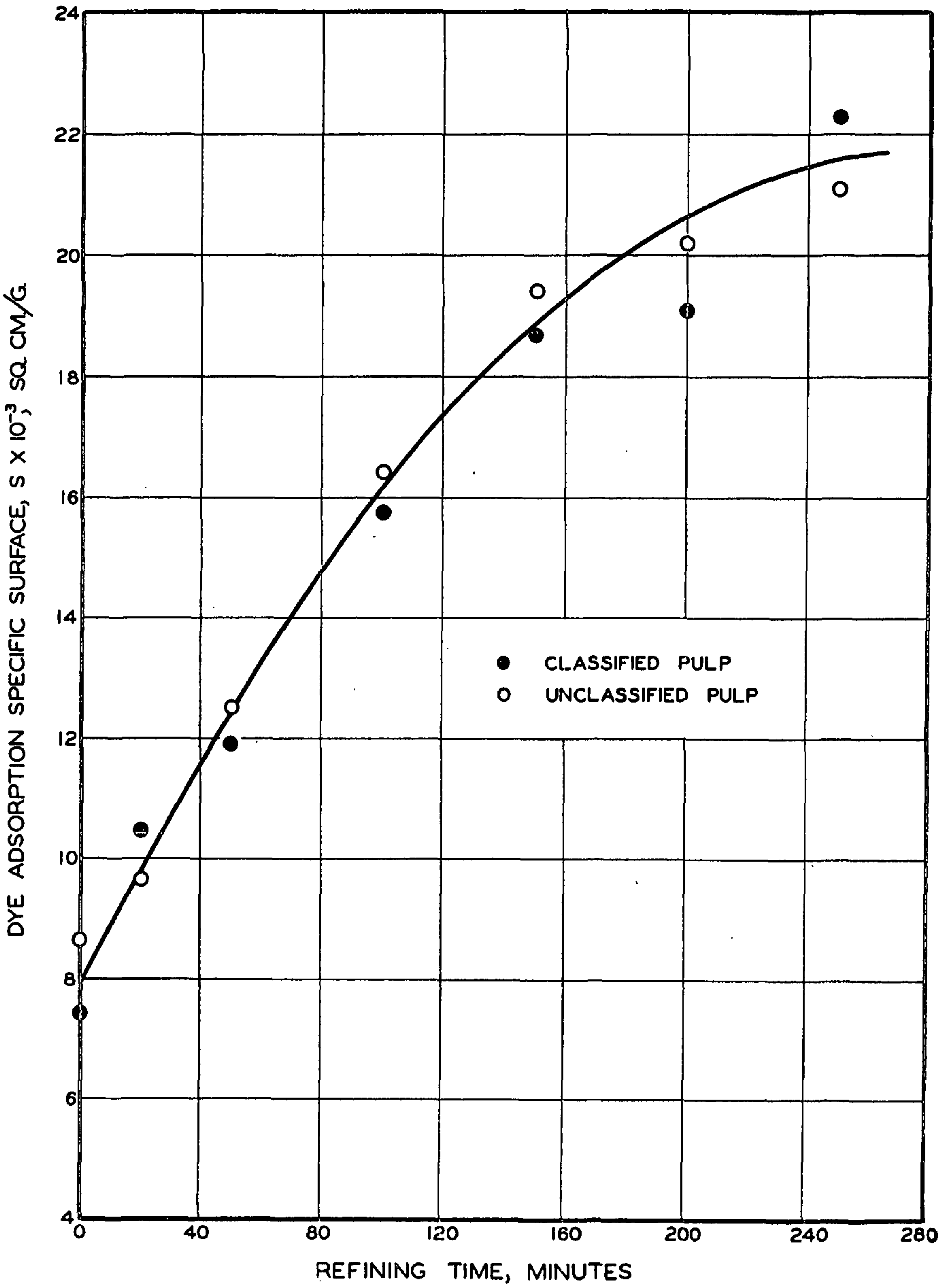

Figure 3

Dye Adsorption Specific Surface as a Function of Refining Time

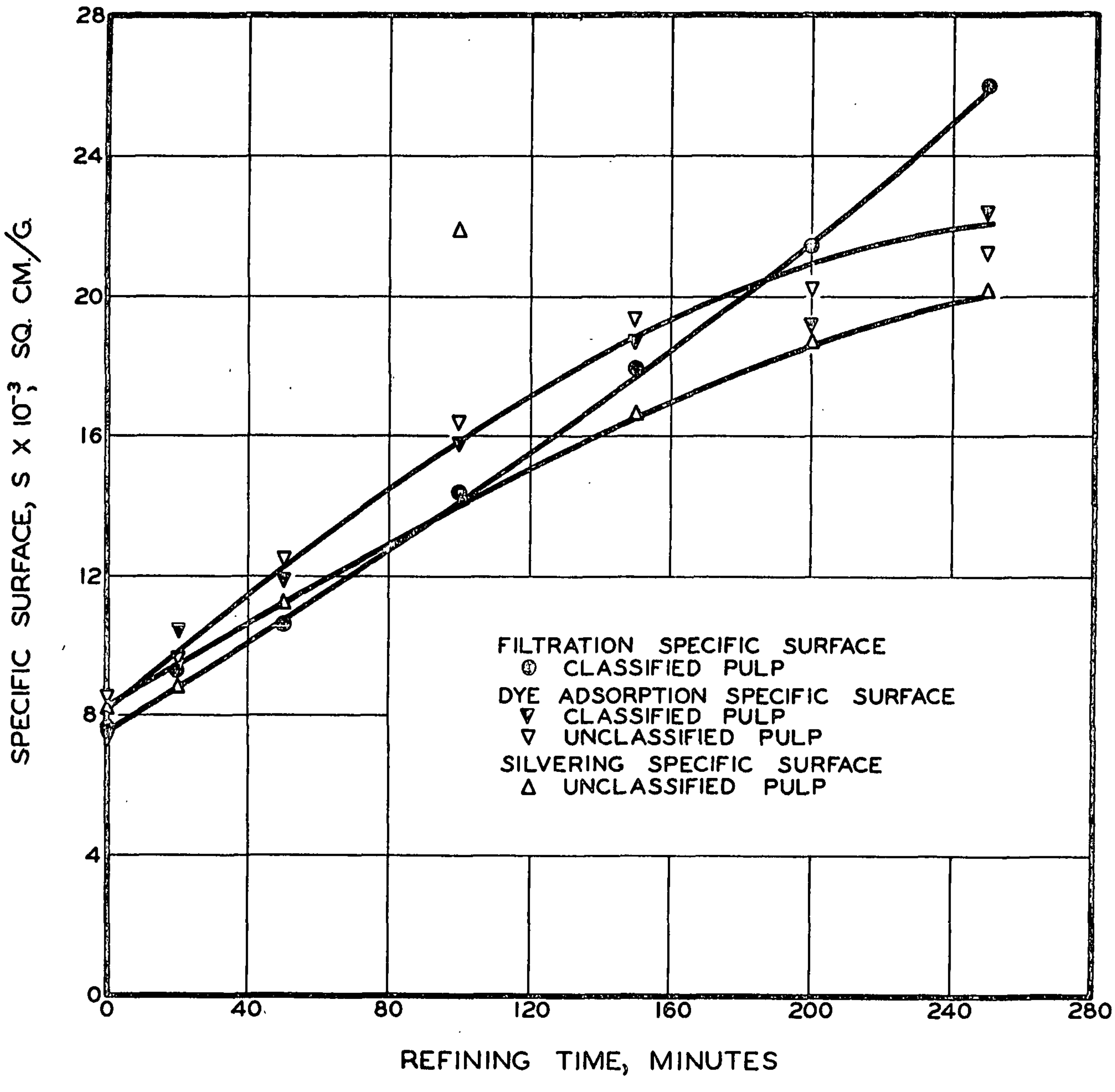

Figure 4

Comparison of Methods for Determining Specific Surface hydrodynamic area of classified pulp (whole fibers with fines removed). In the case of the dye adsorption area, such surface may be much the same as the hydrodynamic surface, but the correspondence might also be purely fortuitous.

As well as the present methods are understood, the physical picture of exactly what surface each determines is not entirely clear. The generalized picture is something like this: (See sketches in Figure 5, A, B, and C; also photomicrographs of 100 min. beaten fibers, Plates C and G.)

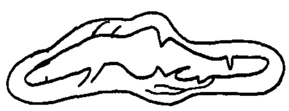

Figure 5A
Fiber Surface Determined by Filtration Resistance

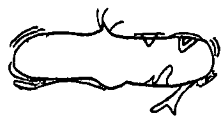

Figure 5B
Fiber Surface Covered by Dye Molecules

Figure 5C
Fiber Surface Involved in Silvering

It may be seen from a comparison of the three sketches that the total volume, per gram dry fiber, (enclosed by the hydrodynamic plane of shear) is larger in the filtration method than in the other two, thus the surface on that basis must be larger. Note, however, that the very fine fibrils are probably encased in the over-all water sheath surrounding a fiber so that the individual area contribution of these may be lost in the filtration resistance experiments. On the other hand, the semigelatinized "webs" of wall material visible in the photograph, Plate G, must contribute enormously to filtration resistance of unclassified stocks.

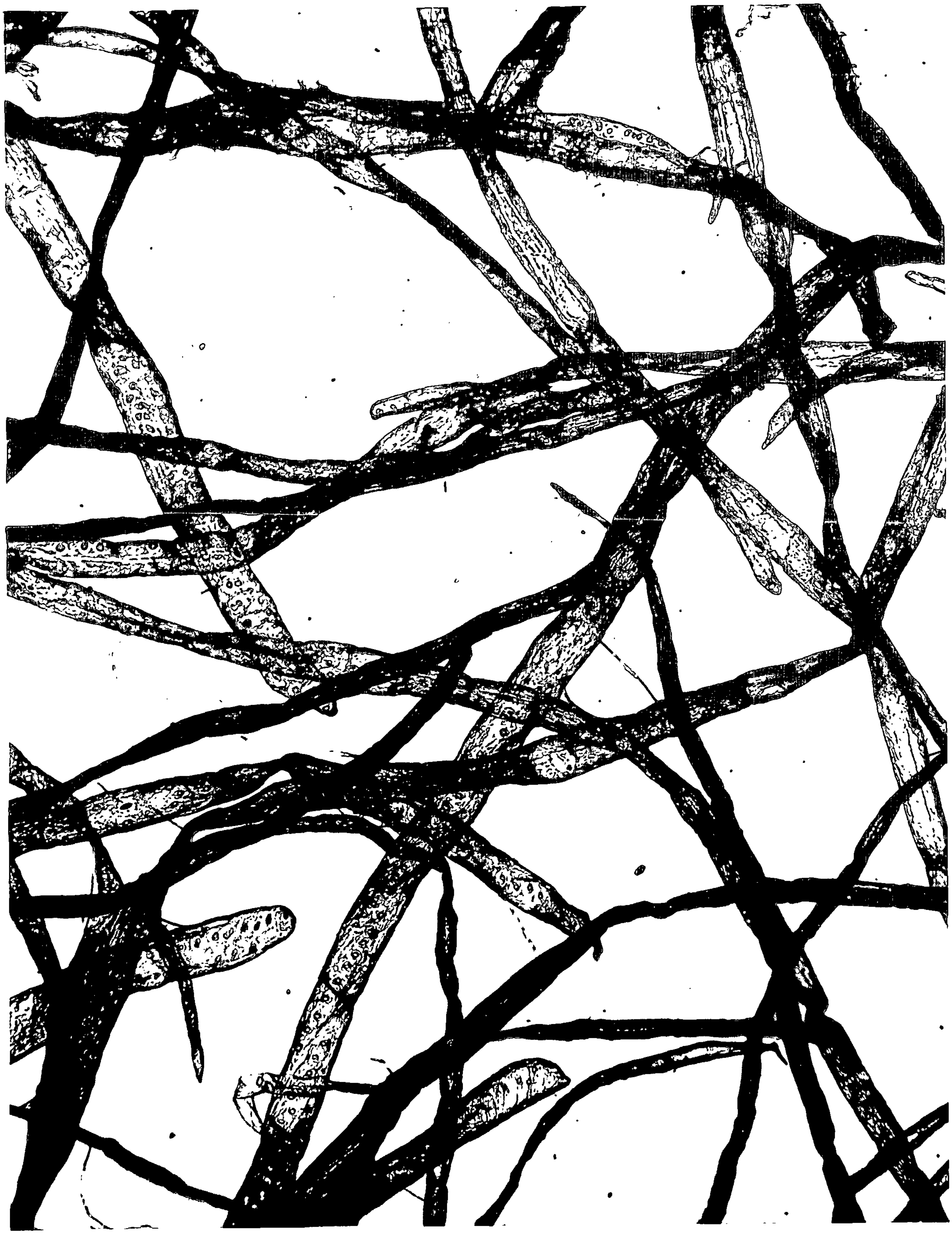

Plate A
Classified Pulp 0 Minutes Refining
150x

Plate B

Classified Pulp 20 Minutes Refining

150x

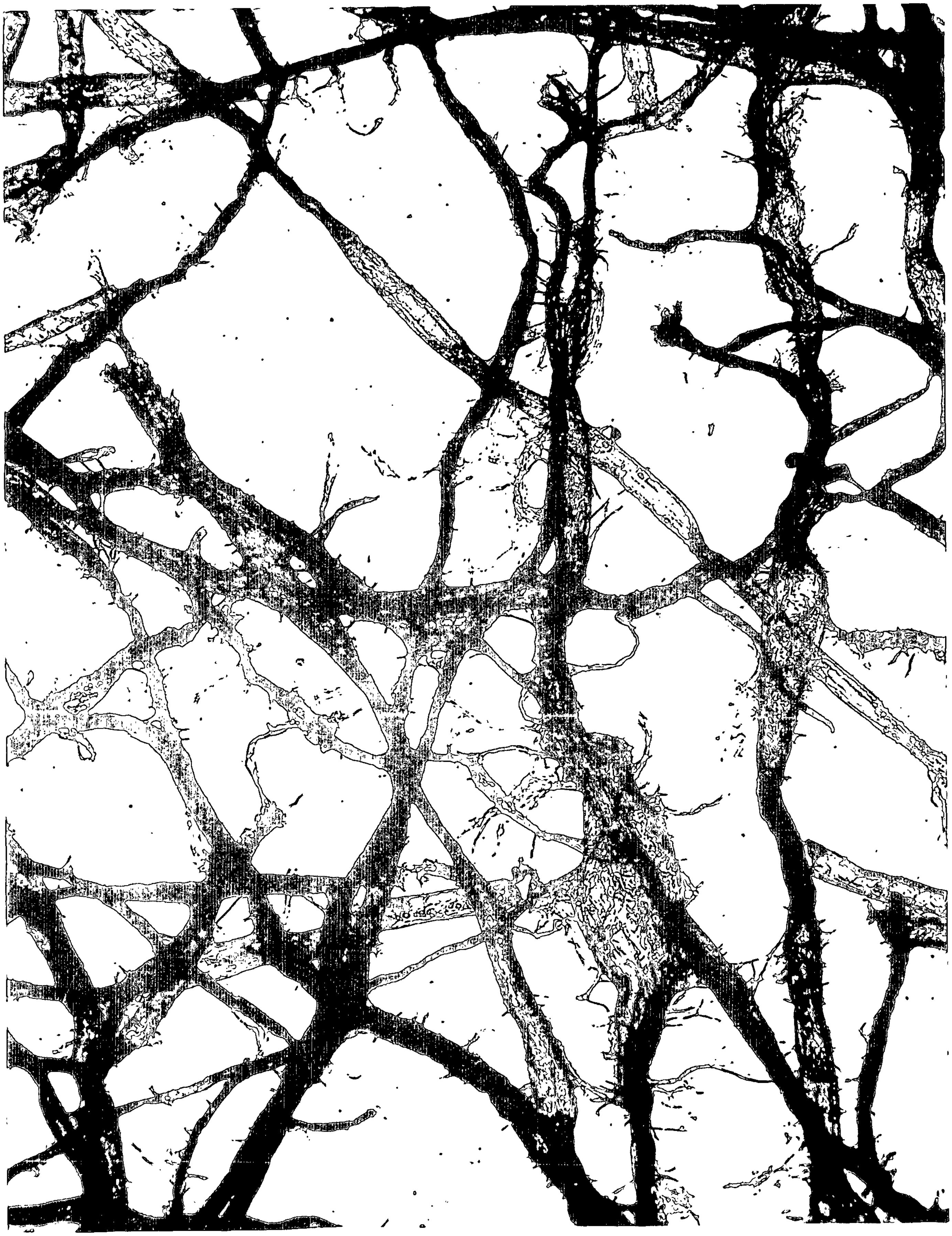

Plate C
Classified Pulp 100 Minutes Refining
150x

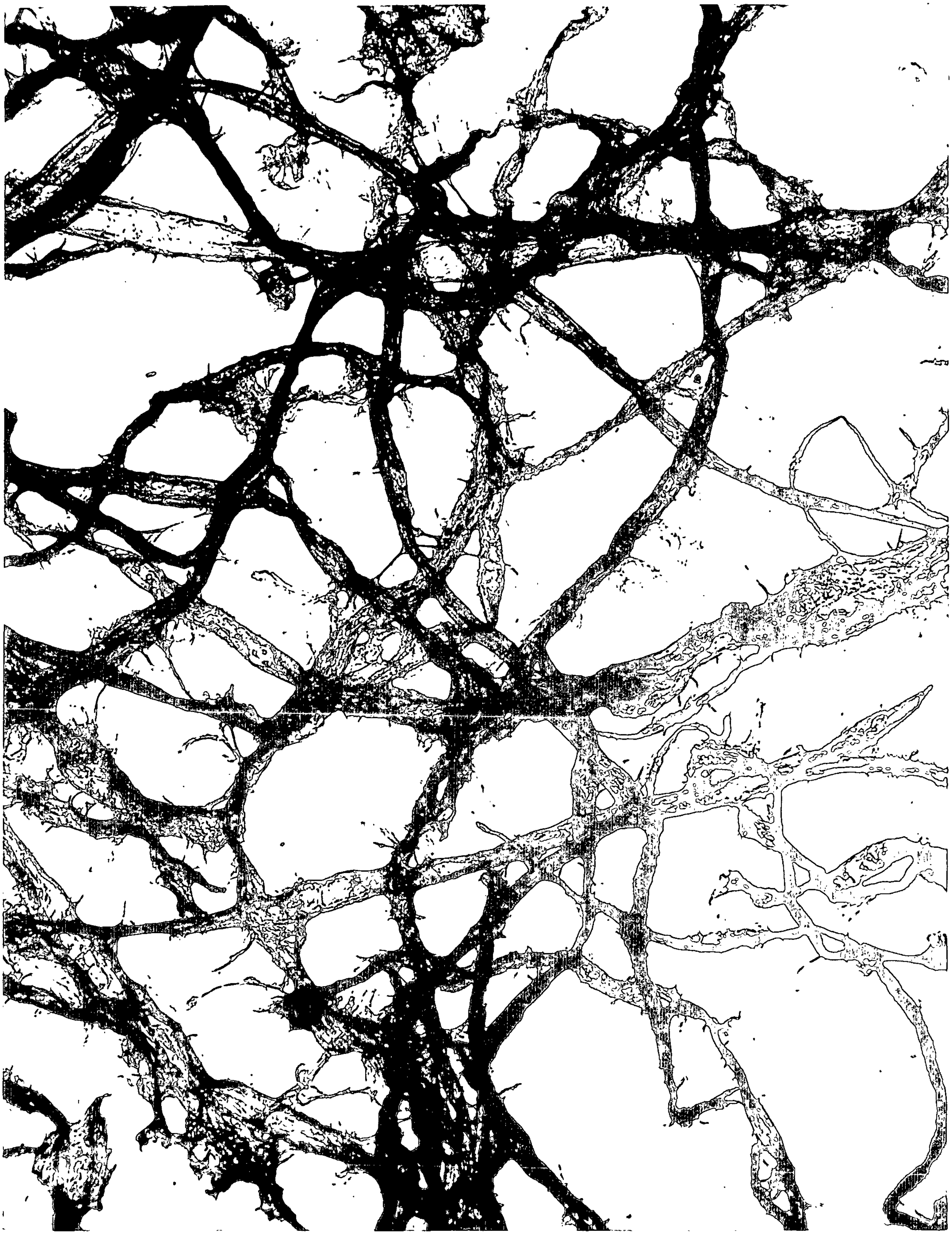

Plate D
Classified Pulp 200 Minutes Refining
150x

Plate E
Unclassified Pulp 0 Minutes Refining
150x

Plate F
Unclassified Pulp 20 Minutes Refining
150x

Plate G
Unclassified Pulp 100 Minutes Refining
150x

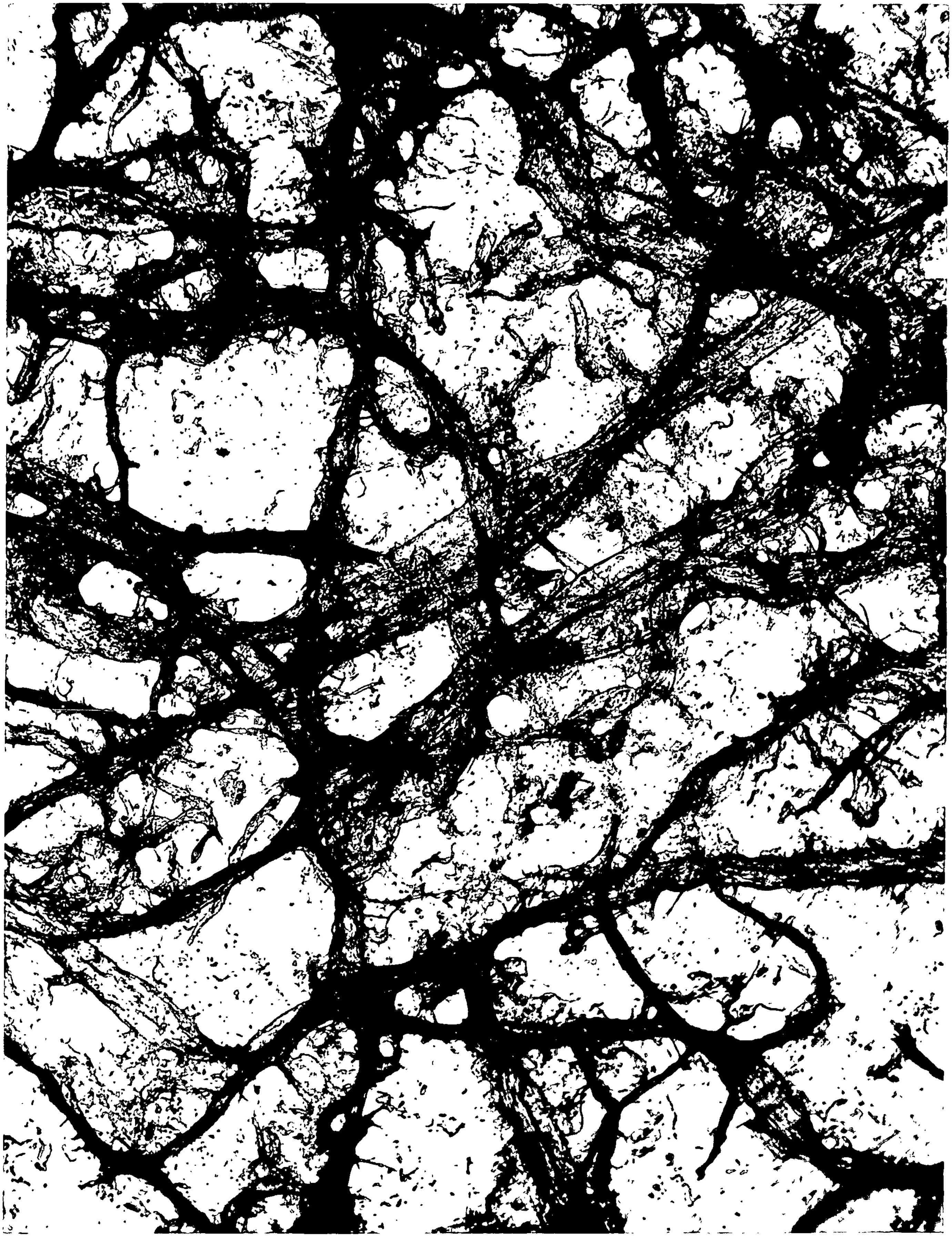

Plate H
Unclassified Pulp 200 Minutes Refining
150x

Turning to the silvering representation, we may see that the fiber is somewhat shrunken by the "denaturing" effect of high temperature and that the silvering deposit has plated over fibrils and microcrevasses alike. Individual particles of fiber "fines," however, will each be plated separately and may have increased catalytic activity. One would speculate from the picture that the silvering method would be slightly low for unclassified pulp and definitely low for classified pulp.

Coming to the dye adsorption picture, note that a layer is shown entering crevasses and covering fibrils retaining fiber identity--the whole surface of the fiber is not covered, but in spots a double layer or multilayer of dye is indicated. It is believed from the experimental evidence that the dye does not take up at all on the "web" material or other debris which has lost fiber identity. By calibrating the dye adsorption against one of the other methods for <u>unbeaten</u> pulp, it is believed that a reasonably accurate value of area (really obtained through compensating variation in the two principal uncertain factors--failure to cover the entire surface and tendency to form multilayers) obtains on <u>beating</u> for classified pulp. This value would be presumed to be smaller than that for the filtration resistance method because of the volume effect previously mentioned. However, the method obviously gives seriously false low values for unclassified pulps.

It must appear obvious that the external specific surface of pulp is not a definable entity. The quantity obtained as a measure of specific surface must depend on the method of measurement; thus the <u>definition</u> of external specific surface (of beaten pulps) is not complete without specification of the means of measurement. The choice of methods to be employed in a given investigation involving surface area would depend on which definition of external surface is important. If the hydrodynamic definition is paramount, the choice of the filtration method is obvious. If adsorption phenomena rule, the dye adsorption method may be preferable. Information presented in this report shows the contributions and limitations of each. The correlation of each with physical properties is given in a later section. Decision of a method of choice must be based on such knowledge plus the requirements of a given problem at hand.

The discussion so far may then be summarized by stating that three different methods of determining the external surface of beaten pulps have been examined and the relative definitions of external surface indicated by each have been compared.

D. INCREASE IN SPECIFIC SURFACE WITH TIME OF BEATING

It is notable that both the external surface of the fibers in the whole pulp, that of the fiber debris, and the total (external and internal) surface of the whole fibers in the pulp increase almost linearly with beating time in the ball mill. Rittinger's Law for size reduction assumes the mechanism of subdivision to be essentially that of shearing and states that the energy consumed is proportional to the fresh surface produced (22). Since the mechanical characteristic of the ball mill is essentially that of constant power input, the energy expended on the pulp is a direct function of time. Thus, the experimental data indicate that Rittinger's Law holds almost perfectly for ball mill beating of pulp.

It has been proposed by Higgins and Harrington (23) that the presence of fines in the beating operation is responsible for the "very low" efficiency of energy consumption on beating. While the energy required, per gram of whole pulp, to produce the surface area represented by the fines is larger than that required for the increase in external surface of the discrete fibers alone, both are overshadowed in order of magnitude by the energy required to produce the additional internal surface developed on beating! In Table IIIA, these figures are compared (assuming Rittinger's Law to hold) on the basis of one hour of ball mill beating of one gram of pulp.

TABLE IIIA

ENERGY REQUIREMENT FOR SURFACE AREA DEVELOPMENT

	Increase in Surface Area, ($m^2/g.$)	Relative Energy Requirement
External - whole fibers	0.4	1.0
External - fines	1.2	3.0
Internal - whole fibers	23.6	59.0

Also, it is instructive to compare Rittinger Numbers (area development per unit work input) for external and total surface with those for mineral size reduction. See Table IIIB.

TABLE IIIB

RITTINGER NUMBERS FOR WOOD PULP AND MINERALS

Material	Apparatus	Rittinger Number (sq. cm./ft.-lb.)
Wood pulp	Ball mill	1255 (total surface)[1]
Wood pulp	Ball mill	98 (external surface)[1]
Quartz	Ball mill	36-94[2]
Quartz	Drop weight crusher	243[2]
Galena	Drop weight crusher	1300[2]

[1] See Appendix C-1 for data and calculations

[2] Reference (22)

It may be seen that the ball mill processing of pulp is no less efficient than ball mill crushing of quartz when comparing external surface developed per unit energy input. Also, if development of internal surface is considered, the ball mill processing of pulp is every bit as economical of power as the highly efficient drop weight crushing of the soft mineral, galena.

It is thus concluded that the processing of pulp is not inherently "inefficient" and that little merit attaches to the proposal that fines be removed before or during processing.

E. RELATIONSHIP BETWEEN SURFACE AREA AND FREENESS

It was shown in Progress Report Thirteen that the filtration resistance data for both classified and unclassified pulp when plotted against freeness both fell on a common "S"-shaped curve. As demonstrated in Figure 6, surface area and freeness also show a common

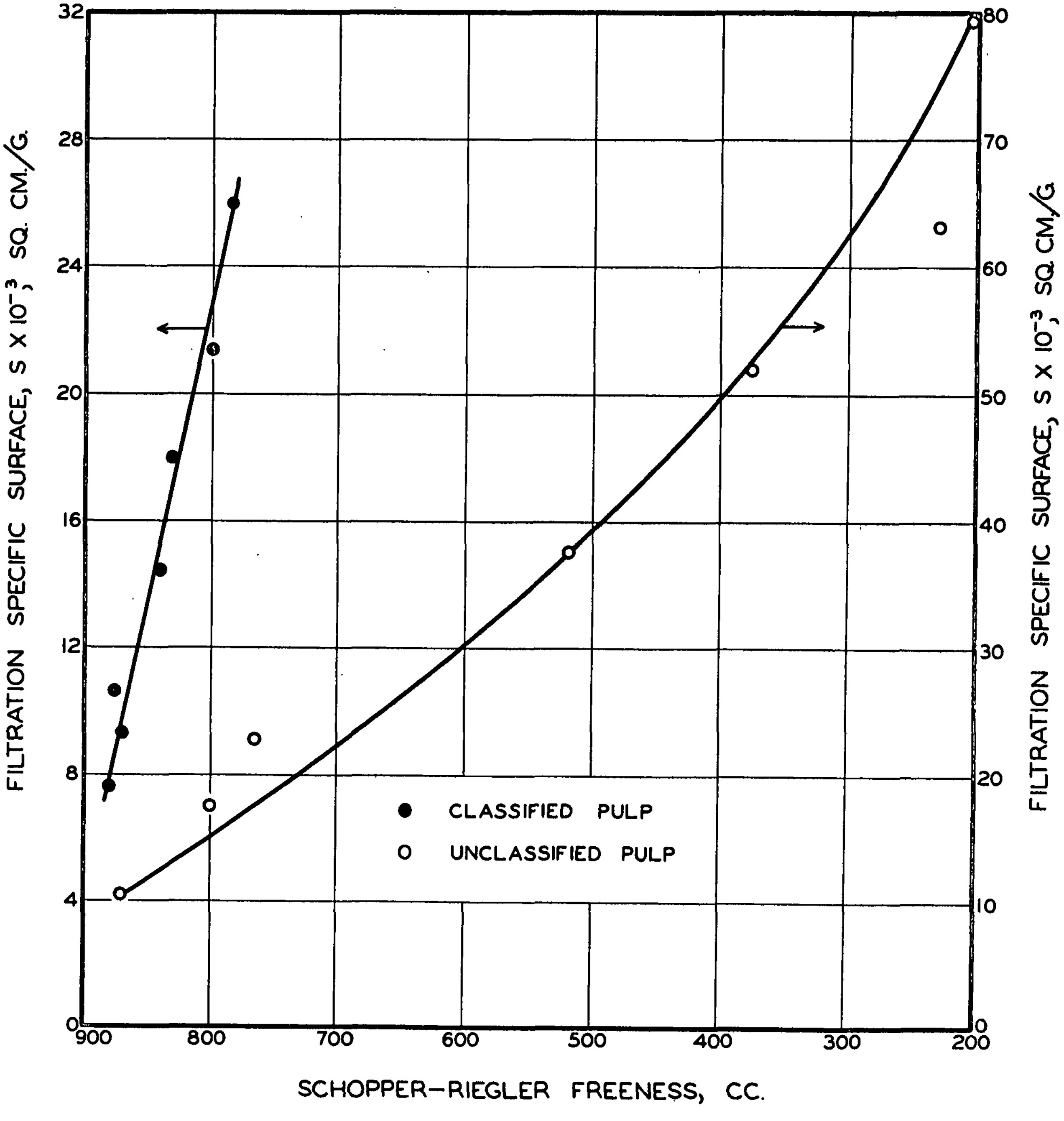

Figure 6

Specific Surface and Freeness Relationship although a complex relationship.

On first sight, these data may lead one to inquire if the freeness test is not thereby justified. It would appear from these data that the freeness test is measuring some aspects of external surface area and thus is at least something of a fundamental test. There are, however, two very important objections to such an interpretation. Firstly, the relationship is obviously a complex one with the great disadvantage that in the earlier stage of the beating process for unclassified pulp (or for classified pulp through the whole range of beating), the freeness test has not appeared to change at all rapidly in comparison with changes in external surface area. As will be shown in a later section, this leads to a fatal insensitivity of the freeness test to surface changes which may presumably cause great strength changes. Secondly, this relationship is not expected to hold, or at least is expected to assume a different function, when methods of stock preparation other than ball mill beating are employed.

It would certainly be fallacious to deny any relationship between freeness test and external specific surface. But it would seem that one is justified in alleging that this distant and complex relationship is a truly negligible value in predicting paper properties related to the fundamental property of external specific surface.

F. CHOICE OF METHOD FOR EXTERNAL SURFACE MEASUREMENT

In evaluating degree of beating, papermakers are often concerned with a variety of problems connected with that fundamental property, the external specific surface. Such factors as the drainage rate, the machine speed, the effectiveness of water removal in the press, the retention of fillers, the retention of dyes and pigments, and the ultimate retention and effectiveness of sizing and other internal additives depend on the external surface of the fibers. Unfortunately, these important factors depend on different aspects of the external surface of the fibers. To some, fines and fiber debris are important; to others, the extent of macerated and crushed or "wet beaten" fibers are important, and to still others, the extent of true fibrillation is paramount. At the moment, no one test--not the freeness test and not even any single one of the three surface area tests here discussed--can entirely sort out the variables. A combination of tests suitably contrived can help in sorting out the situation, and if one is dealing only with one specific aspect of surface development, one may possibly rely on a single surface area measurement or type of measurement.

It may be well to examine some of these specific requirements and how the presently available tests fit into these requirements:

The factors of <u>drainage rate</u>, the effectiveness of <u>water removal</u> at the <u>presses</u>, and the effectiveness of water removal on the <u>driers</u>, all of which bear on the machine speed, are obviously related to the hydrodynamic surface of the fibers. It would appear that filtration resistance measurement on pulp in this situation should thus tell the papermaker what he needs to know about the external surface of the stock. However, this statement may not be made completely categorically. While knowledge is advancing rapidly on the connection between filtration resistance and the obvious operation of filtration which takes place on the wire, knowledge has not advanced as rapidly in the area of water removal at the presses or, for that matter, on the drier. It is possible, for example, that press and drier effectiveness depends not only on the gross filtration resistance of the stock but also on how much of it is contributed by fines and how much by the maceration of the total fibers themselves. Thus, surface area determinations may have to be supplemented by fiber length distribution information in the prediction of pressing and drying properties.

The question of filler retention is, of course, much more complex. Here it is doubtful that best filler retention is obtained in the situation where the surface area is generated primarily by fines. At least superficially, it would appear that maximum crushing and fibrillation of fibers is what would promote good filler retention. If a single test were to be useful here, possibly the dye adsorption test for surface area comparison is what one would choose.

When we come to the topic of dye retention, strangely enough, the dye adsorption test is not necessarily the method of choice. It is perhaps obvious that the freeness test is no indication whatsoever of the shade which one will obtain in a given sheet of a given dye formula. The actual shade or depth of color that one will get even with a single dye depends not only on the total amount of surface but on the kind of surface. Many dyes, for example, adsorb preferentially on the fines so that the amount of color per unit weight of fiber is much greater in the fines fraction than in the whole fiber. This often results in two-sidedness, in that the top side of the sheet where fines are retained will appear much darker, because of the higher concentration of dye, than the bottom side of the sheet from which fines have been washed through the wire.

Some dyes have the reverse action to what has been mentioned above; the dyestuff, Color Index 327, used in the dye adsorption test, is one of these. By reverse action, we mean the dye preferentially takes up on whole fibers and takes up very little, or possibly not at all, on the fines. This, too, can lead to two-sidedness, in that with a pulp with a larger amount of fiber debris, the shade will actually be darker on the wire than the felt side of the sheet.

If pigments are also present, or fillers, the color situation is still further complicated because the shade obtained will depend not only on the retention of the dye, but on the retention of the filler and on the respective affinities of fiber and filler for the dyestuff. In this complex situation, surface area tests can be of greatest value, first in pointing out the desirable selection of components of a dyeing formula to avoid problems brought on by variation in the performance of stock preparation equipment. Secondly, the tests can also be of value in determining the source of trouble when unexplained variations in shade occur from day to day, shift to shift, or beater to beater. It would seem that both the filtration resistance and dye adsorption tests, together with a fiber classification, would really be required for a scientific analysis of problems arising in this area.

In connection with the <u>retention</u> of <u>sizing agents</u> and other <u>beater additives</u>, it is important to point out that not only the total amount of external surface and its distribution among the fiber components is important, but also the electrokinetic and other physico-chemical surface characteristics of these various surfaces must be considered. The initial stages of pickup of size precipitate appear to be a matter of adsorption of a complex precipitate on the surfaces of the fibers. It is of course recognized that this mechanism is enhanced, or assisted, by the mechanical entrapment of the floc of precipitate. The mechanism of takeup of wet-strength resins, as presently understood, is rather definitely an adsorption at the surface. In the case of the melamine resins, the adsorption mechanism results in an undue concentration of the resins in the fines and a consequent loss, in normal machine operations, of some of the added materials. The same difficulty applies to the use of certain polysaccharide beater additives for strength improvement.

It would thus appear that for maximum effectiveness of the beater additive, the fines present in the system should be minimized. If not minimized or controlled, the level of fines should be accurately known so that appropriate excess active ingredients may be added should the fines level rise significantly. It would thus seem that a control based on the filtration resistance method plus a fiber classification, or on a combination of filtration and dye adsorption surface area, would be quite necessary to the obtaining of the consistent and economical performance of many of the beater additives. It may further be seen that here is another instance where the freeness test would be completely useless. It is easy to conceive of a situation where changes in refining equipment would occur, producing more fines and less maceration. At a given freeness in such case, even though strength properties would not be greatly affected, the distribution of beater additives between the fibers, where it is needed, and the fines, where it is wasted, might be so badly thrown off as to greatly reduce the effectiveness of the beater additives.

The purpose of this part of the discussion has been to raise questions as to the effectiveness of the present method of control in the several operating areas affected by external specific surface. It has also been the object of this discussion to indicate that the "degree of beating" does not necessarily mean the same thing when one is comparing, say, strength properties, drainage rate, and retention of beater additives. That being the case, changes made on the basis of a single control test with a view to correcting a drift of one property from the specification limit may have an unnoticed adverse effect on the other properties. Hence comes the third object of this discussion--to point out the possible utility of certain basic measurements on the external surface area plus fiber classification in a complete scientific analysis of such a complex problem.

G. CONCLUSIONS

It has been demonstrated in this work that the filtration resistance method of determining external specific surface may be used with great confidence. The possible utility of the rather empirical dye adsorption method of estimation also has been explored.

In the discussion of this information, the possible applications to process control of surface area determinations have been covered. With our improved knowledge of the virtues and limitations of the various methods of external area measurement, it is possible to state with considerable confidence the conditions under which they will yield useful results in technical investigations.

In a brief survey of the problem of energy expenditure for surface development during beating, it has been shown that the refining of pulp is not different from the common size reduction operations in this regard.

(Conclusions as to implications of surface area data with regard to sheet strength are presented in Section VIII of this report.)

V. STRENGTH PROPERTIES - GENERAL CONSIDERATIONS

A. SUMMARY

In this section the interrelationship of the various strength properties is critically examined, especially with regard to the effect of fines. It is shown that fines have but little effect on tensile and burst but a marked effect on velocity-viscosity product and folding endurance. The important concept that there are several different materials in the fines fraction is placed in perspective. Attention is drawn to the presumed importance of a "cementing substance" in the fines fraction.

The controversial subjects of freeness and apparent density as criteria of pulp strength are reexamined. Although neither is a basic measurement, both have the virtue of being readily performed. It is shown that the freeness test has a basic weakness which is difficult to ameliorate in its oversensitivity to fines. Apparent density does show some prospect of usefulness if its sensitivity to changes in fiber length distribution may be allowed for.

Also shown in this section are representative correlations of strength properties with surface area development of the pulp. The implications of these correlations are discussed.

B. INTRODUCTION

Of paramount consideration in the interpretation of the integrated studies is a recognition of the peculiar character of ball mill beating. To review, the ball or pebble mill was selected as the beating engine for these studies because of the reproducibility of beating afforded by this device. Another reason for the choice is that the ball mill produces practically solely fibrillation and crushing in contrast with the varying amount of cutting action found with beaters and refiners. It is recognized that a certain amount of cutting is essential for maximum strength development. But it was felt that as a first step in the analysis of variables of beating, it might be well to study the somewhat less complicated process of ball mill beating.

In this connection, the point must be repeated that the material commonly referred to as "fines" must indeed comprise a number of components physically and chemically differing from one another. These components include (1) true, discrete, fine fibers, (2) ray cells and similar wood residues, (3) cell wall debris and other fine solid particles without morphological fibrous character, and (4) a colloidal dispersion of resinous and carbohydrate material. For the sake of future discussion, let us argue that the fines from the <u>ball mill beating</u> of sulfite pulp doubtless contain but a very small amount of discrete fine fibers and are largely composed of cell wall debris plus colloidal substance. This is in contrast with the fines from an ordinary beater or refiner, which doubtless produces considerable <u>fine fibers</u>. It is assumed that the major differences between pulp properties observed in this investigation and those observed in previous investigations employing laboratory beaters may be accounted for by the difference in the character of the fines.

C. STRENGTH PROPERTIES AS A FUNCTION OF BEATING TIME

In Figures 7 through 13 are displayed the correlation of the various physical properties of handsheets with time of beating for both

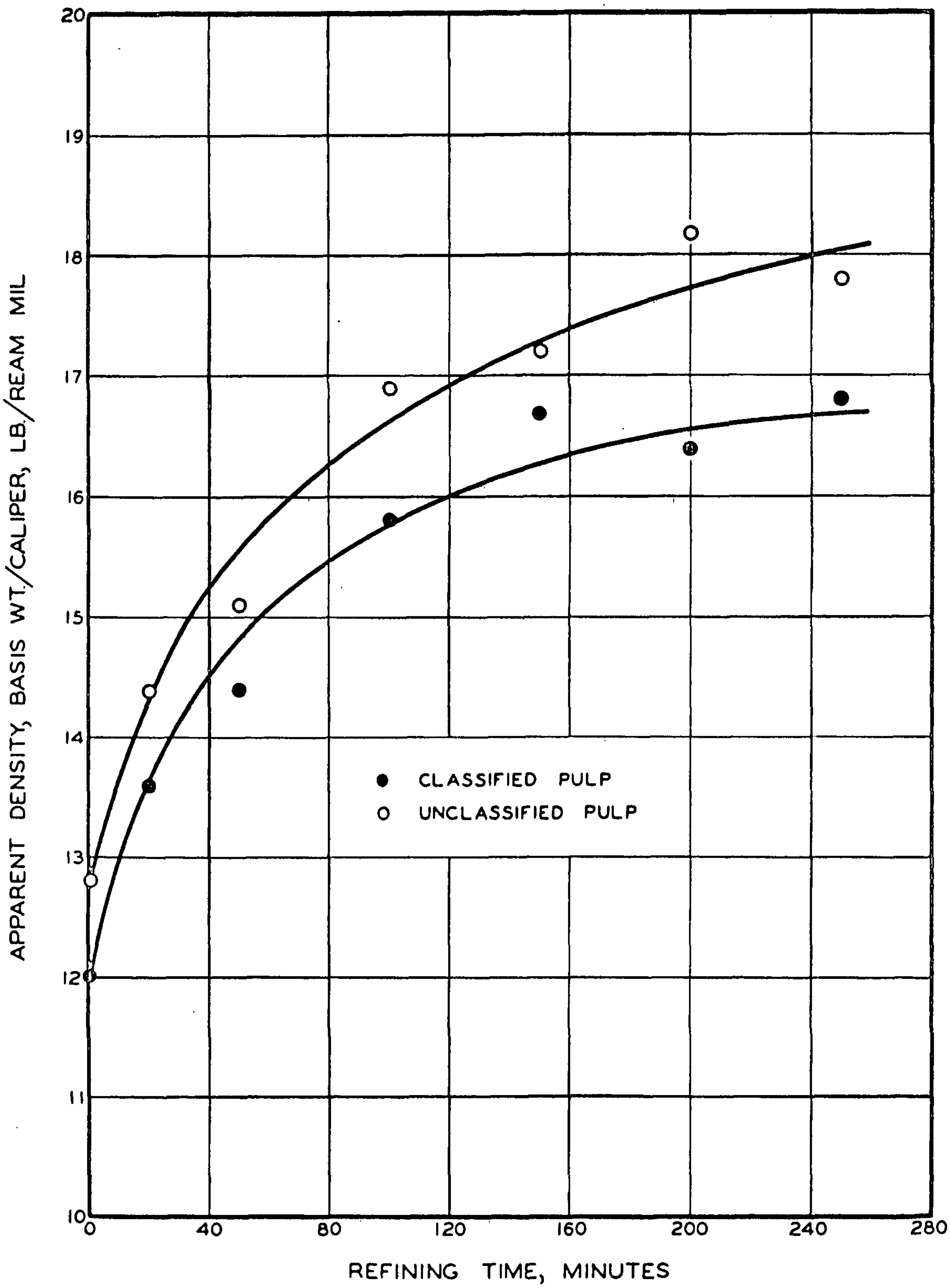

Figure 7
Apparent Density as a Function of Refining Time

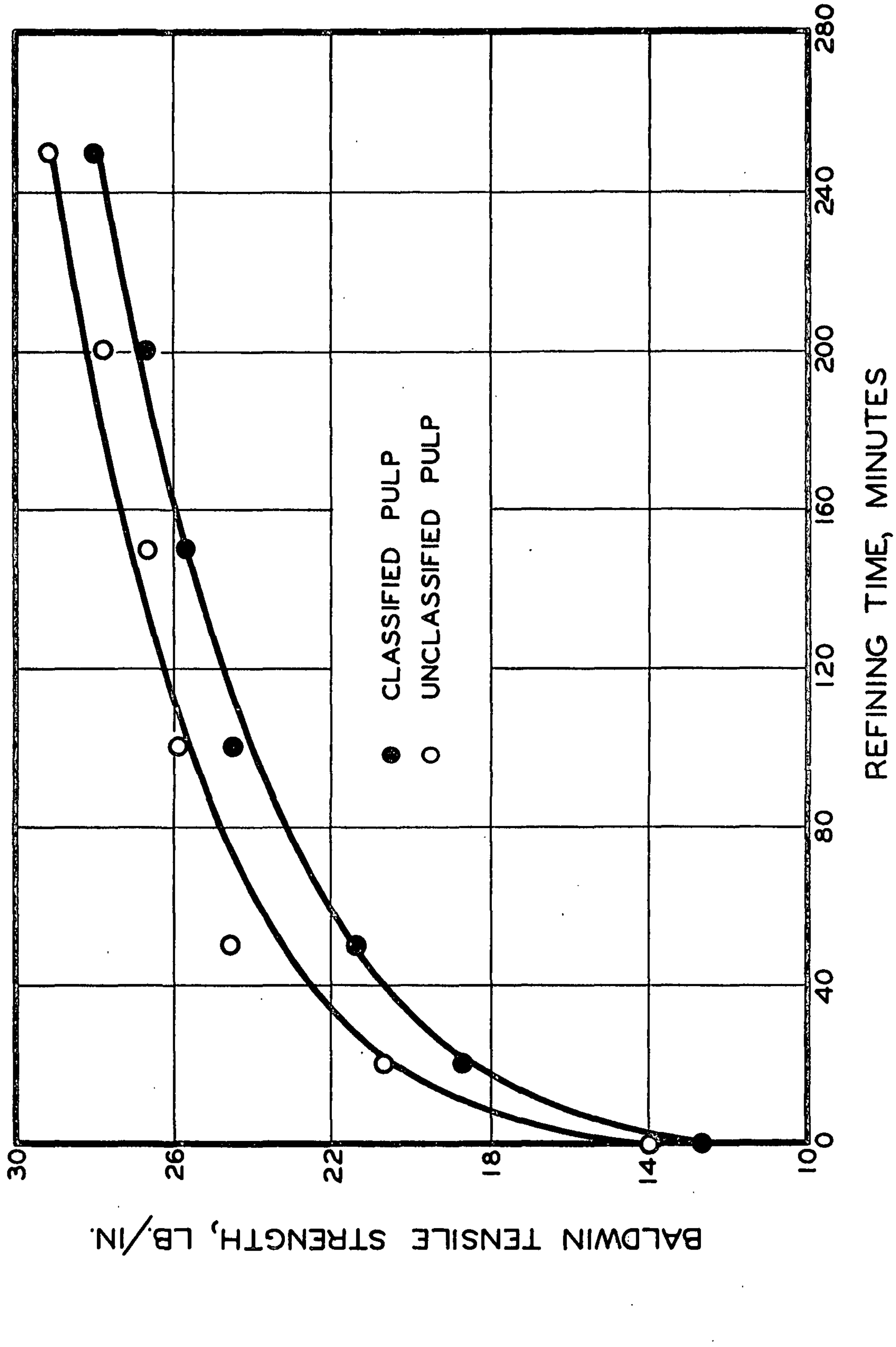

Figure 8

Tensile Strength as a Function of Refining Time

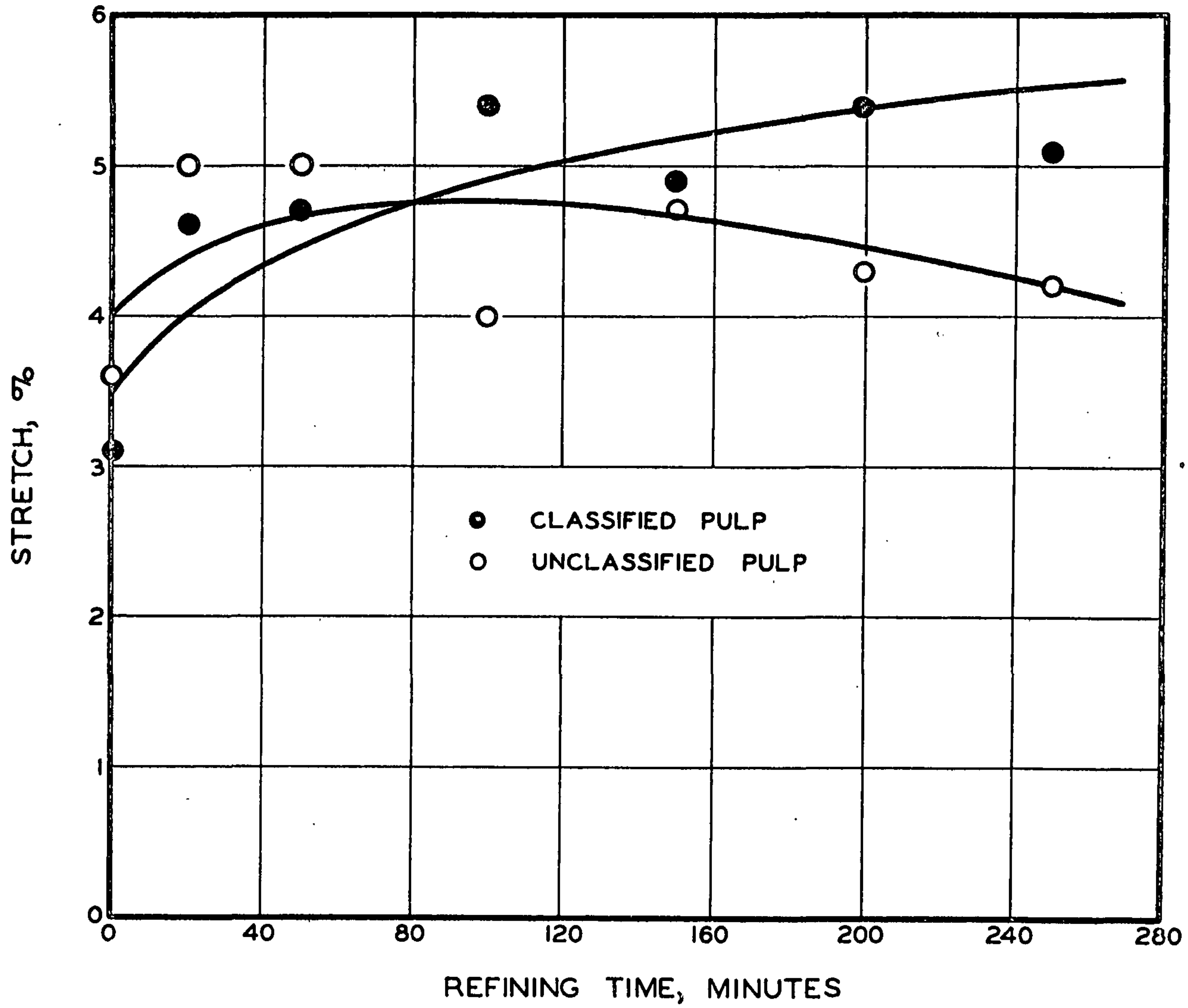

Figure 9

Stretch as a Function of Refining Time

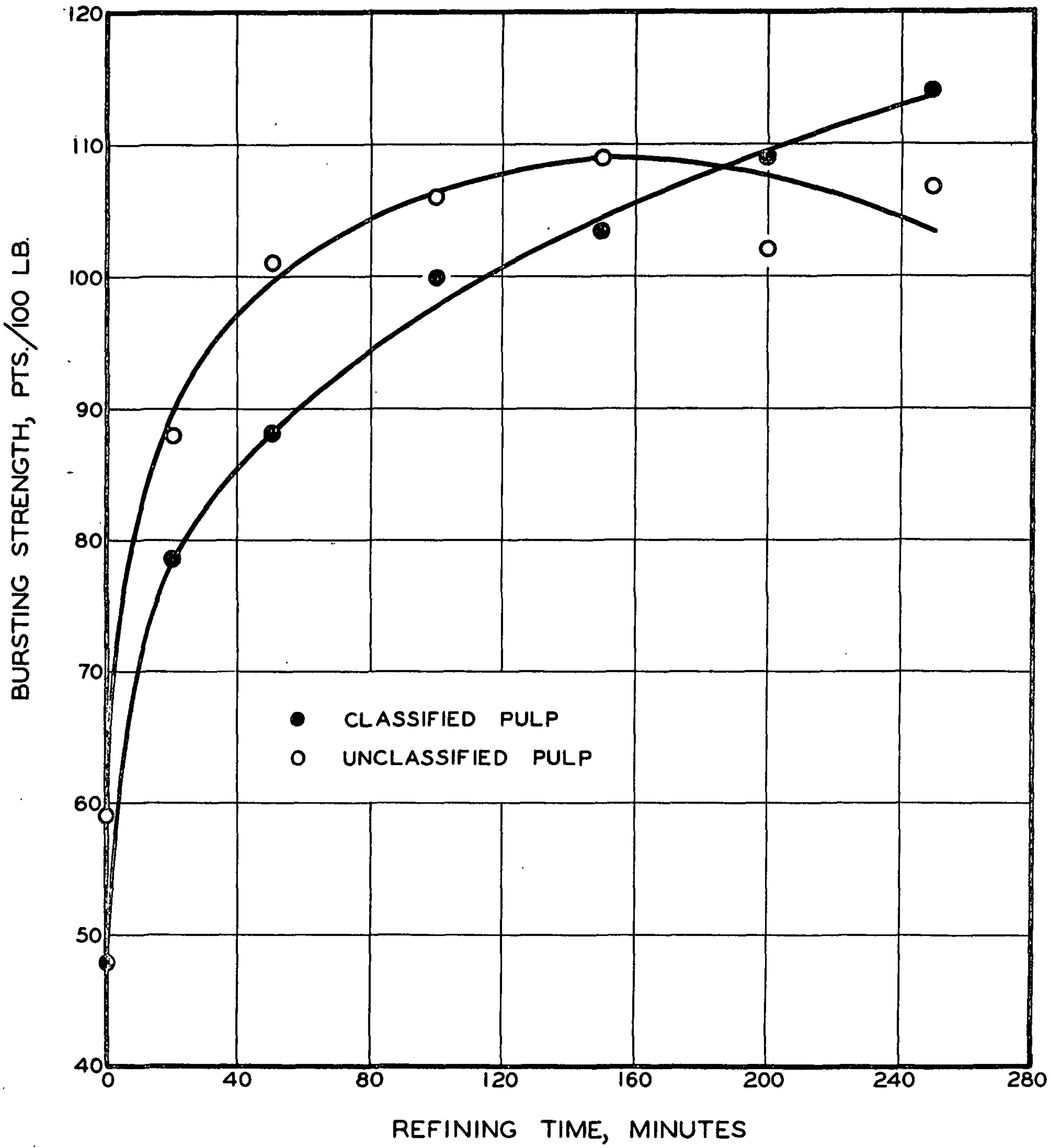

Figure 10
Bursting Strength as a Function of Refining Time

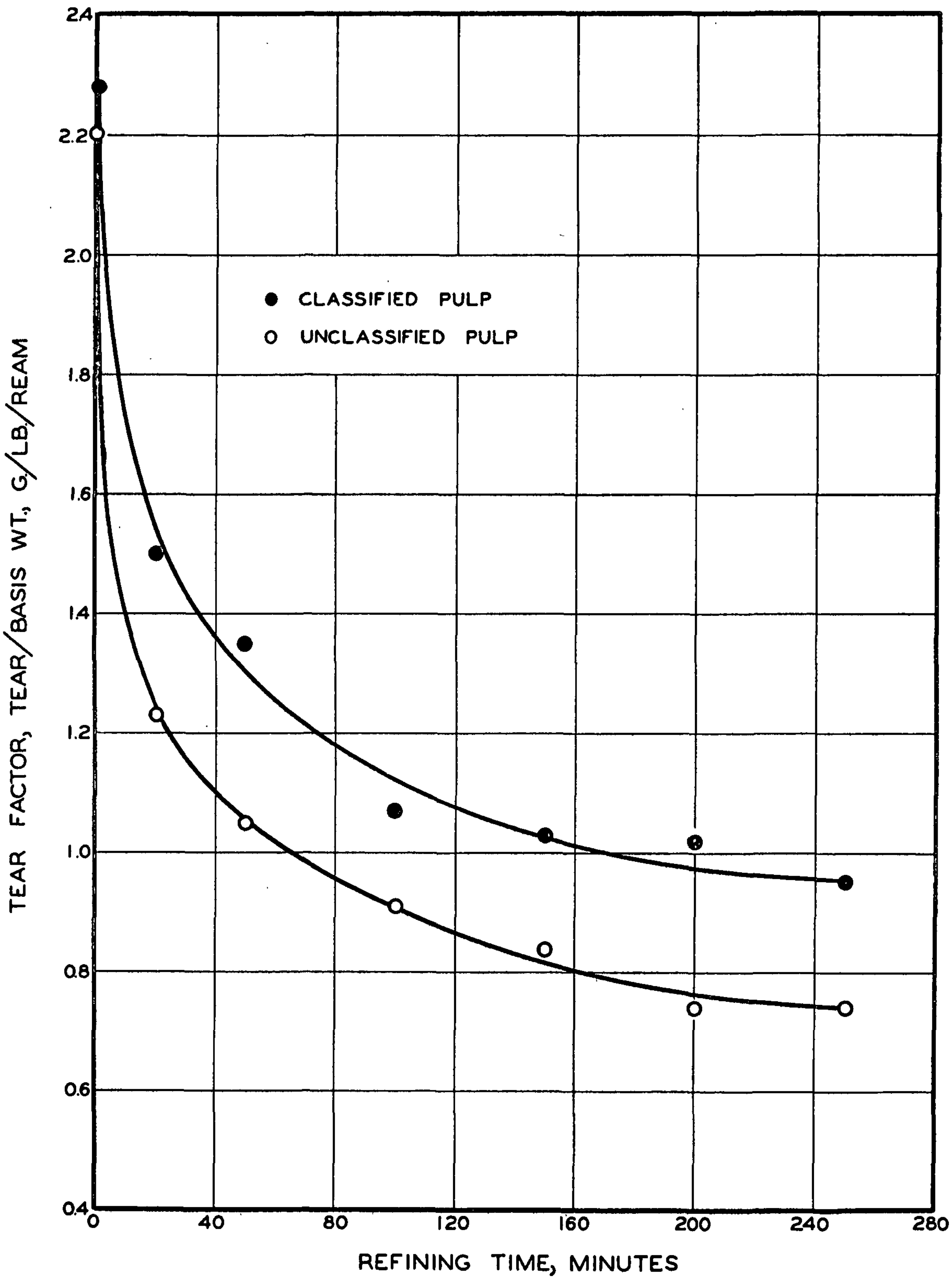

Figure 11

Tearing Strength as a Function of Refining Time

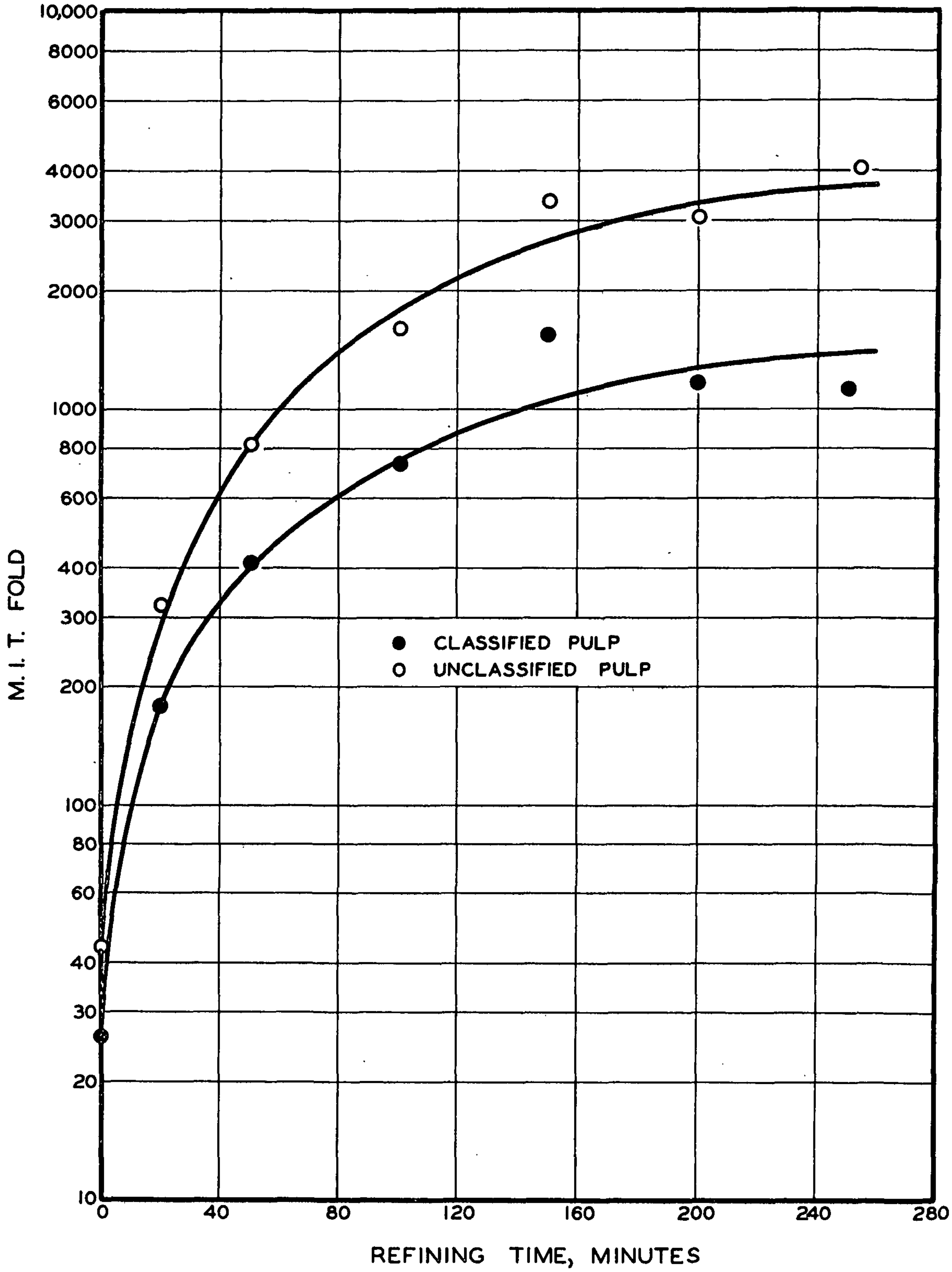

Figure 12

Folding Strength as a Function of Refining Time

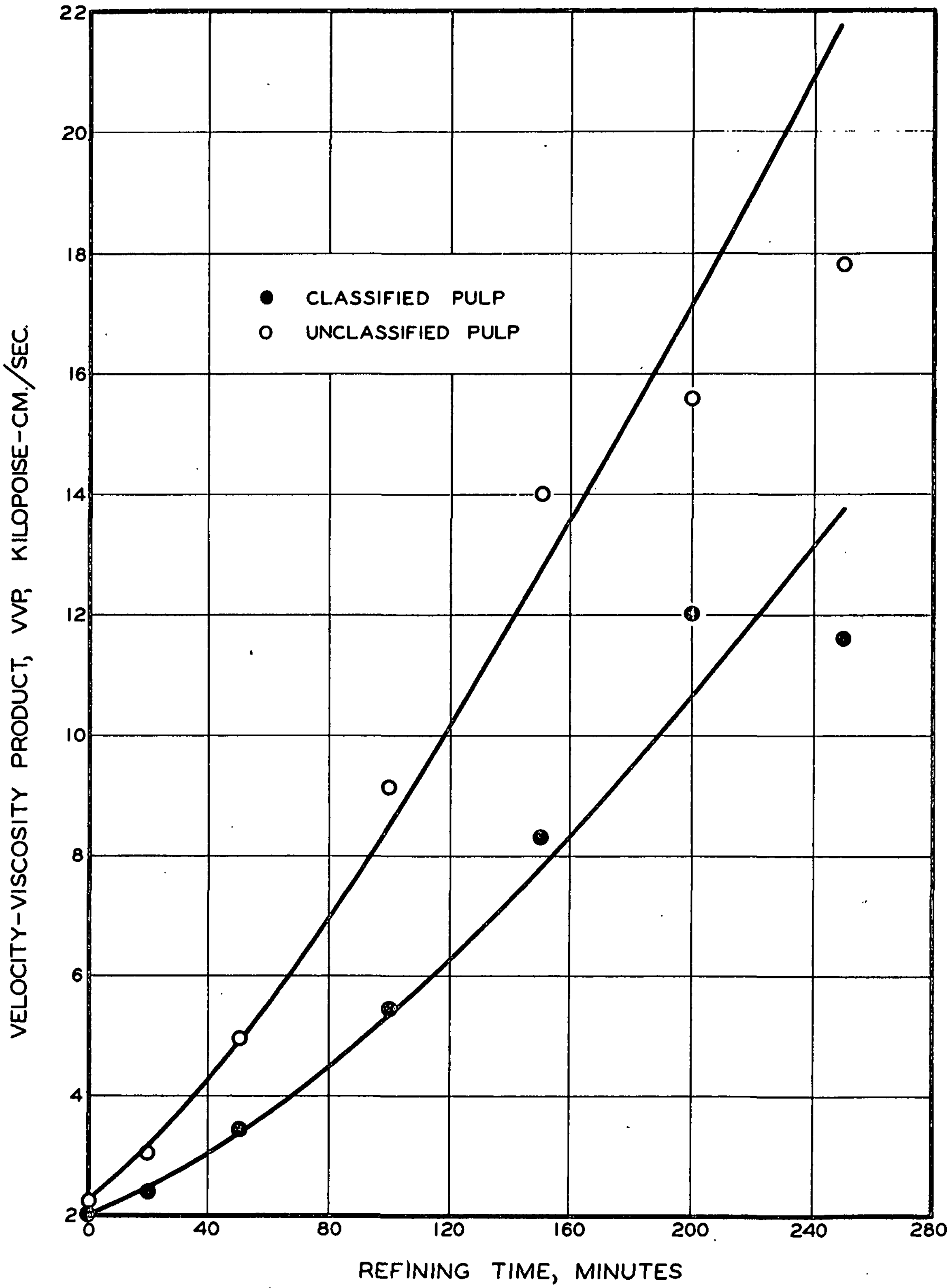

Figure 13

Velocity-Viscosity Product as a Function of Refining Time the classified and unclassified pulp. A quick survey of these data immediately revealed how complicated the interrelationships of the various physical properties may be.

For example, in contrasting the well-known and well-standardized burst and tensile tests, it may be seen that the simpler tensile test is but little affected by the fines removal on classification and that a regular increase of tensile strength with beating time persists through the entire 250 minutes of beating. On the other hand, burst, in the early stages of beating, shows a much greater loss in strength upon fines removal than does the tensile. Furthermore, in the later stages of beating, it appears that the peak of burst has been reached for unclassified pulps but the peak has not been reached for classified pulps. Thus at 250 minutes beating time the pulp from which the fines have been removed is stronger than the whole pulp. A glance at the stretch data betrays the reason for this. It is known that burst is primarily a function of tensile strength and stretch. It may be seen that the stretch of the classified pulps is considerably higher in the later stages of beating than is the stretch of the unclassified pulps.

Turning now to tear and apparent density (plotted on rectangular co-ordinates as a function of beating) and to the fold and velocity-viscosity product data (plotted on semilogarithmic co-ordinates as a function of beating time), we note a consistent effect of fines removal on strength properties. In all of these cases, the trend of the data for the classified and the unclassified pulps is in the same direction and the curves have about the same shape for a given parameter. The trend of all these data inescapably points toward the existence of something like the "cementing substance" once popularly regarded as being responsible for paper properties, as in truth being at least partially so responsible. The comparatively great effect of fines removal upon the values of fold and velocity-viscosity product as contrasted with the relatively small effect on tensile strength strongly points to this conclusion.

Tensile strength, after all, is largely a matter of the exercise of the inherent fiber strength of the components of the paper with the aid of interfiber bonds. The velocity-viscosity product, on the other hand, certainly has little or nothing to do with strength of fibers, and the fold test depends to a much larger degree upon how well the fibers are cemented together than upon the ultimate strength of the fibers.

The considerable difference in apparent density of pulps with and without fines also supports the case for a cementing substance. The much lower density, one might say the "fluffed up" appearance of the sheets prepared from classified pulps, betrays the presence in the sheets from <u>unclassified</u> pulp of a substance capable of internal compression of the sheets.

An examination of the photomicrographs of the classified and unclassified pulps demonstrates quite graphically the point raised above. If one looks at the photograph of unclassified pulp at the 100-minute beating interval (Plate G), one may perceive the existence among the fibers of areas which are either gelatinized material in film form or extraordinarily thin layers of unravelled wall substance. Whether it be unravelled wall substance or released gelatinized material, the substance is bound to be very highly hydrated and bound to serve as a remarkably effective cementing agent upon drying of a sheet of paper. Now, one may see from Plate C that this substance is almost totally absent from the classified fibers. Whatever its origin, the action of the classifying process apparently disrupted and largely removed the material.

There can be no doubt from the physical data that the loss of such material is responsible for profound changes in these strength properties of the sheet. The fact that such changes do not greatly influence the important variables of tensile strength and burst should not distract us from the significance of this observation. We must go back to the fact that the method of beating here employed was likely optimum for the production of such bonding substance and that the variation in condition of beater tackle in commercial procedures may result in the production of more or less of such substance from time to time and from machine to machine. The implications of this on the whole picture of the piece of paper cannot be ignored; it is felt that they must be carefully considered in future studies of the beating process.

D. APPARENT DENSITY

For some time, workers such as James d'A. Clark (24) have suggested that the rather simple variable of apparent density may be very useful in the evaluation of pulp properties. The data and allegations in the literature on this point are quite confusing and, notwithstanding the fact that Progress Report Five of Project 1513 (25) categorically dismisses apparent density as a useful criterion, it was felt that this matter was worthy of re-examination.

In Figures 14 through 17 are plotted, respectively, tensile strength, velocity-viscosity product, M.I.T. fold, and tear for both classified and unclassified pulp as a function of the apparent density of the sheet. In the case of the latter two variables, the data for the zero beating interval have been omitted. Consistent with its previous method of plotting, the fold data were plotted semilogarithmically as a function of apparent density. It may be observed that the smooth data for each of these variables produce a good straight line as a function of apparent density. It may also be seen that there is a slight difference in slope between the data for the classified and unclassified pulp but particularly in the case of the fold data, the difference is slight indeed.

It appears from these data alone that the simple determination of basis weight and caliper should suffice for the prediction of properties of a given pulp when processed in the ball mill. This would, of course, be true only for a given run on a given pulp, but there is the possibility that a given <u>type</u> of pulp will usually show the same correlation between apparent density and strength properties of the sheet upon ball mill beating.

Now, this good straight-line relationship displayed by the data of this study did not show up in the series of beater tests reported in Progress Report One (<u>26</u>) on this project. Two reasons for this suggest themselves: (1) the difference between the ball mill and the beater and (2) some difference in response of the various pulps. In order to partially check this, data from Table II-2, runs 18 and 19 of Progress Report One (<u>26</u>) have been replotted in Figure 18, showing

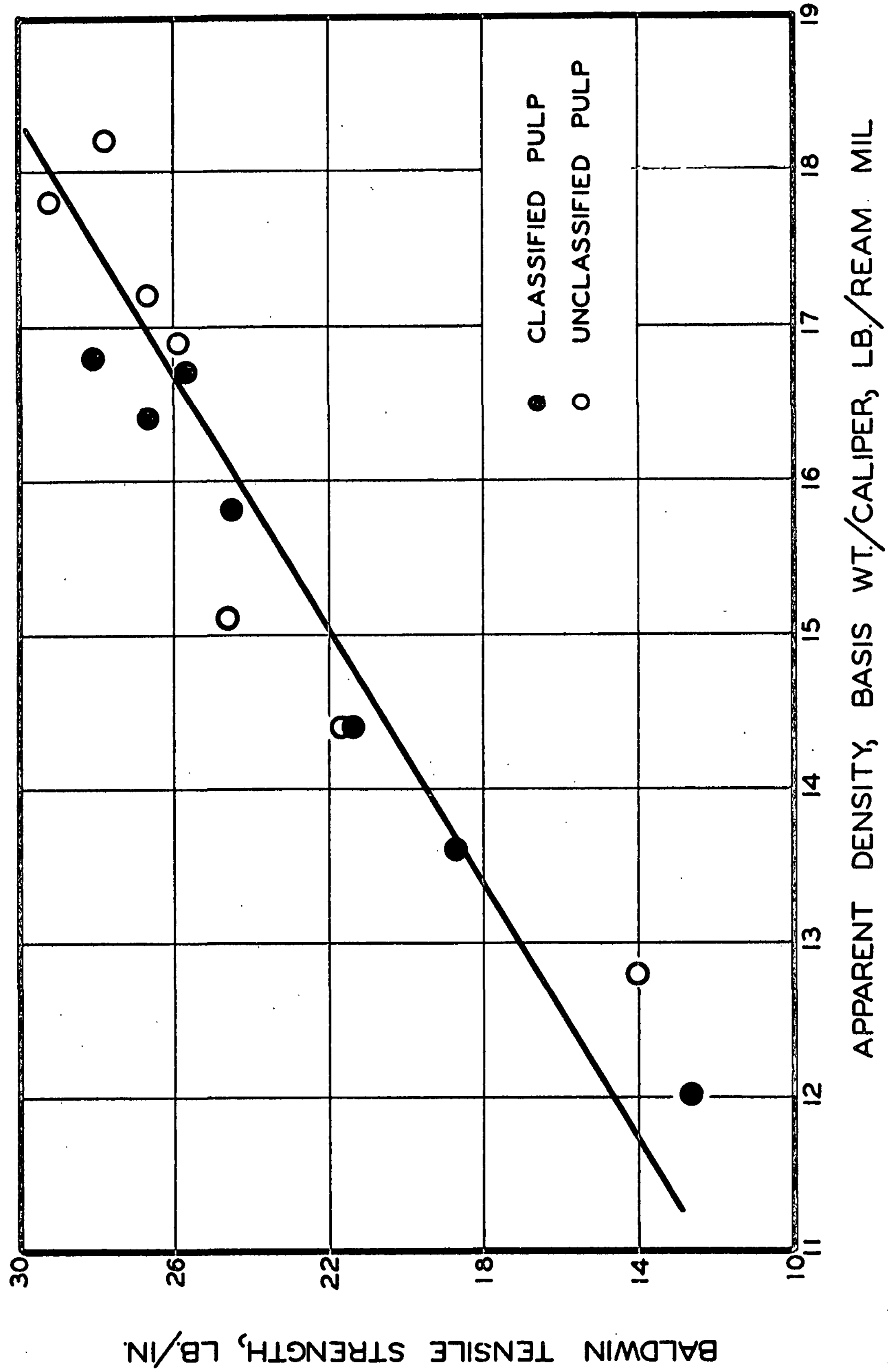

Figure 14

Tensile Strength as a Function of Apparent Density

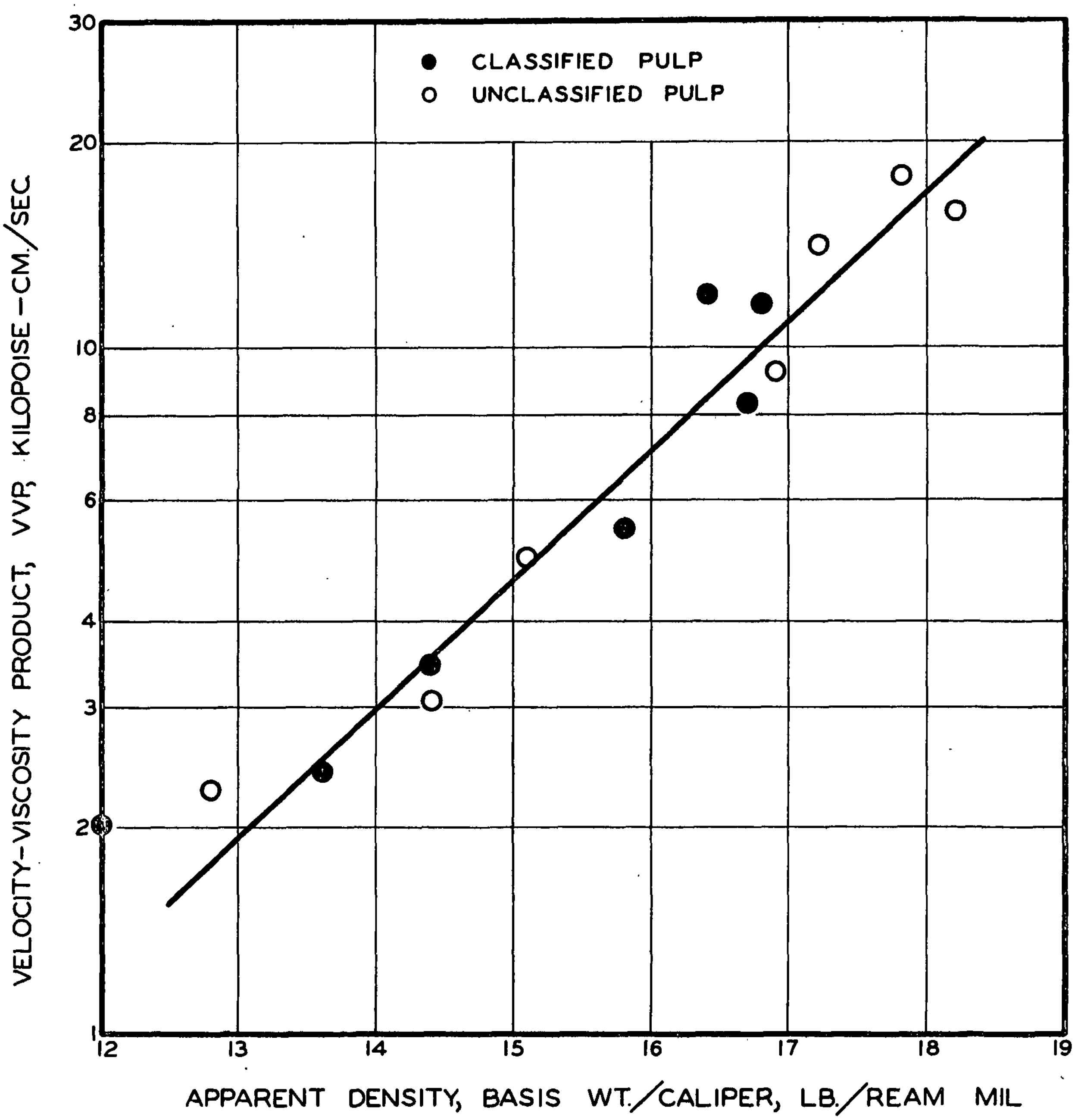

Figure 15

Velocity-Viscosity Product as a Function of Apparent Density

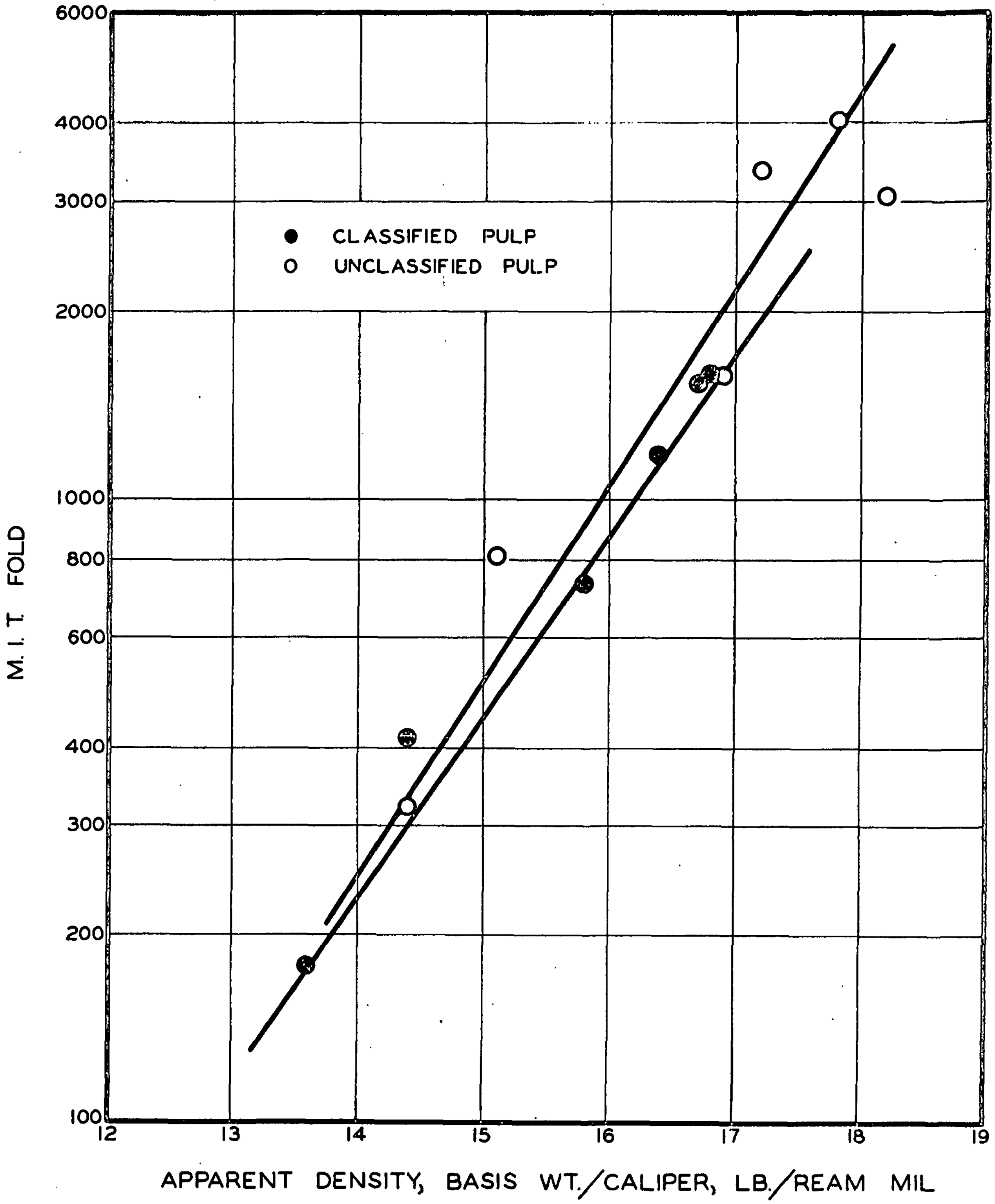

Figure 16
Folding Strength as a Function of Apparent Density

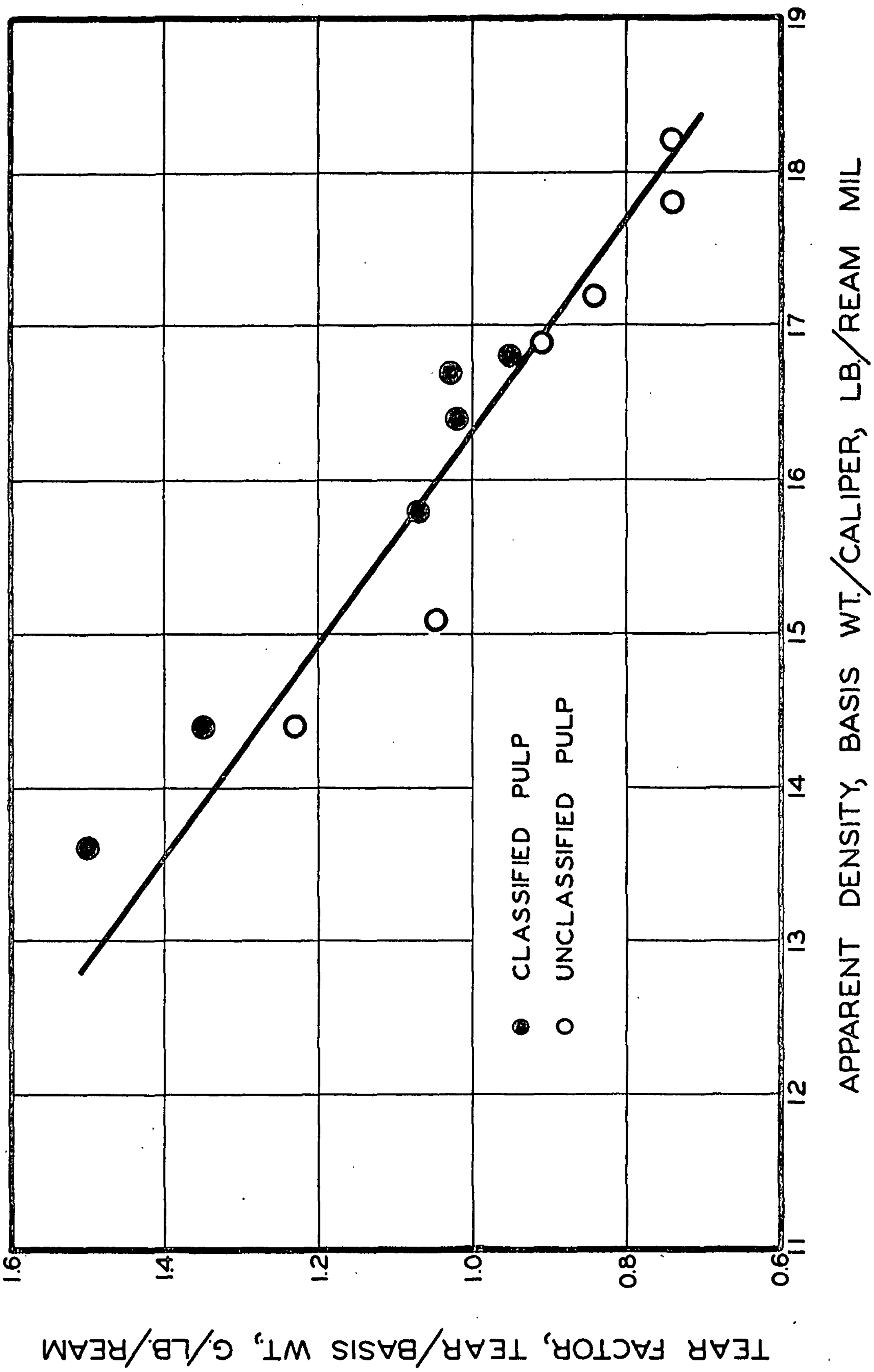

Figure 17

Tearing Strength as a Function of Apparent Density

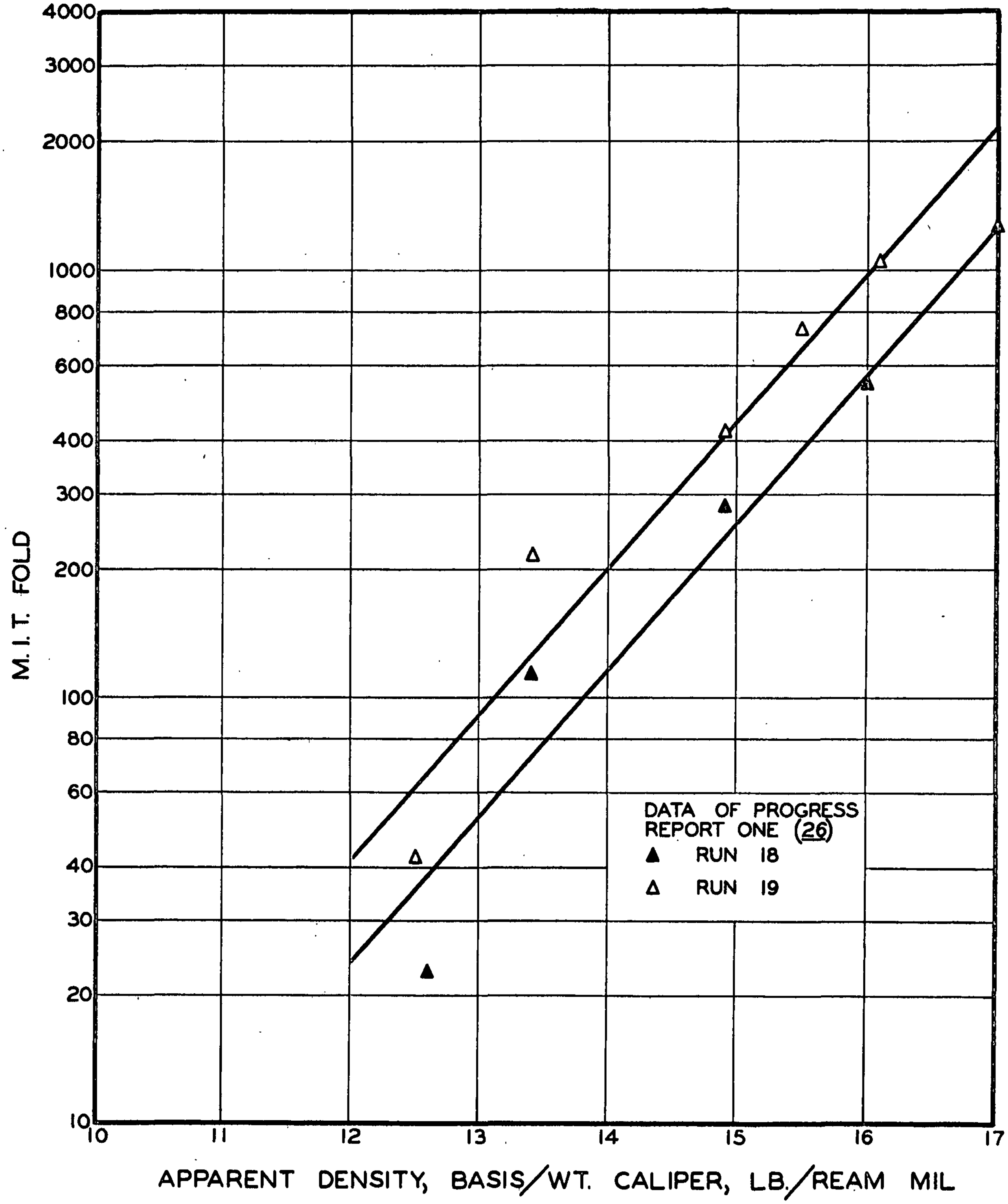

Figure 18

Folding Strength (Progress Report One)
as a Function of Apparent Density

the relationship between M.I.T. fold and apparent density with the same co-ordinates as Figure 16 for the data from the current investigation. These two pulps, no. 18 and 19 of Progress Report One, were similar to that used in the integrated studies; both of these were western hemlock sulfite pulp. It may be seen that the fold vs. apparent density relationship is a good straight line on semilogarithmic co-ordinates but slightly displaced from the line for our pulp material. It is the thought now that the reasons why apparent density did not show up well as an evaluation variable in the previous experiment were a matter of possible overbeating of some of the pulp studied plus the as yet unexamined critical differences between ball mill and beater processing.

Even so, the earlier data on apparent density may be reexamined and valuable information discovered therefrom. For example, in Table IV are listed the various categories of pulp studied in Progress Report One and the freeness and tensile strength values obtained at a point on the beater curve for each sample corresponding to an apparent density of 14. It may be seen that the various types of pulps appear to be well characterized as to tensile strength by comparing all at apparent density 14. For example, the ten individual samples of bleached southern pine kraft pulp differ by no more than ±2 units from the mean value of tensile strength at apparent density 14. A similar spread is observed for the smaller number of the weaker sulfite pulps and the stronger unbleached kraft samples.

In any discussion of what is the "strongest" pulp, there must be agreement as to what "strong" means. For example, it has been

TABLE IV

TENSILE AND FREENESS VALUES OF VARIOUS COMMERCIAL PULPS AT CONSTANT APPARENT DENSITY

Pulp Category	Sample Number[1]	Freeness,[2] cc., S.-R.	Tensile,[2] lb./in.	
Unbleached kraft	22	310	34	Mean = 34.4
	23	300	34	σ = 1.5
	24	450	33	
	30	500	37	
	33	800	34	
Bleached southern pine kraft	1	500	28	Mean = 28.2
	2	500	28	σ = 0.9
	3	450	28	
	4	450	29	
	5	500	29	
	6	500	28	
	7	500	28	
	8	550	29	
	15	375	26	
	21	500	29	
Misc. bleached softwood kraft	16	550	32	
	17	700	35	
	20	720	34	
	27	650	32	
	31	450	37	
	32	650	26	
Bleached pine sulfate	34	350	21	
	35	250	16	
	36	300	30	
Bleached hardwood kraft	26	750	24	
Mitscherlich, foreign	9	650	35	
	10	700	19	
	14	700	22	
Unbleached sulfite	11	750	29	
Bleached softwood sulfite	12	700	20	Mean = 22.1
	13	600	21	σ = 1.2
	18	650	22	
	19	650	23	
	25	650	23	
	28	750	23	
	29	800	23	

[1] As listed in Progress Report One (26)

[2] At apparent density 14, interpolated from Table II-2, Progress Report One (26)

popular to compare pulp strength at a given freeness because freeness was thought to be an indication of drainage rate on the machine. The papermaker would like to know what strength he might expect at that point of refining he needed to use to operate his machine effectively. Since freeness is not necessarily related to drainage rate on the machine and since strength at a given freeness is not necessarily an indication of the ultimate strength a pulp will develop, the writers considered such a comparison of strength properties of pulp as being invalid.

Apparent density has the same attractive features as has freeness: it is very simple to perform. It has the same drawback: it is not a fundamental test. In comparing the strengths produced or producible by different pulps, such factors as fiber stiffness, bonding strength, and history of compression will affect the apparent density figure. Thus, it is not the suggestion of this report that apparent density be considered as a fundamental criterion in pulp evaluation.

It is the suggestion of this report that apparent density be given further consideration as a handy empirical evaluation tool. It is suggested that the controlled experiments here reported show that apparent density has probable value as such a simple evaluation tool if employed as part of a battery of tests for pulp strength prediction.

E. INDICATIONS FROM PHYSICAL TEST CORRELATIONS

The indications of the portion of the integrated studies here discussed are clear in at least two areas. Firstly, the study of a beating process in which pure fibrillation takes place has revealed the importance of some sort of "cementing substance" to the strength properties of paper produced from the beaten pulp. Classification of this pulp with removal of the very fine fraction has produced changes in strength properties wholly consistent with such a concept. It is suggested that this situation may be clouded where other refining techniques are employed to produce more fiber cutting and possibly a significant amount of true fine fibers in the "fines" fraction. It is further believed that a greater appreciation of the respective roles of fibrillation and the development of surface on the one hand, and the production of these fines and cementing substances on the other, will develop from this work.

Secondly, this beating experiment, uncomplicated by fiber cutting, has largely demonstrated at least some of the circumstances in which apparent density can serve as a useful yardstick in this evaluation of the beating process. It is suggested that this variable of apparent density can be made useful in the comparison of pulp from various sources and, furthermore, can be made useful even for beating processes in which the apparent density does not appear a linear function of strength properties of the sheet. It is thought that in a suitable combination with other tests, of fundamental significance, apparent density may take its place as a useful pulp evaluation tool.

F. CORRELATION BETWEEN STRENGTH PROPERTIES AND EXTERNAL SPECIFIC SURFACE

The gross correlation between the strength properties of tensile and velocity-viscosity product and external specific surface as measured by these three different methods may be observed in Figures 19 through 24. Because of the effect of fines, it is to be noted that, in general, two different curves may be observed relating to the given

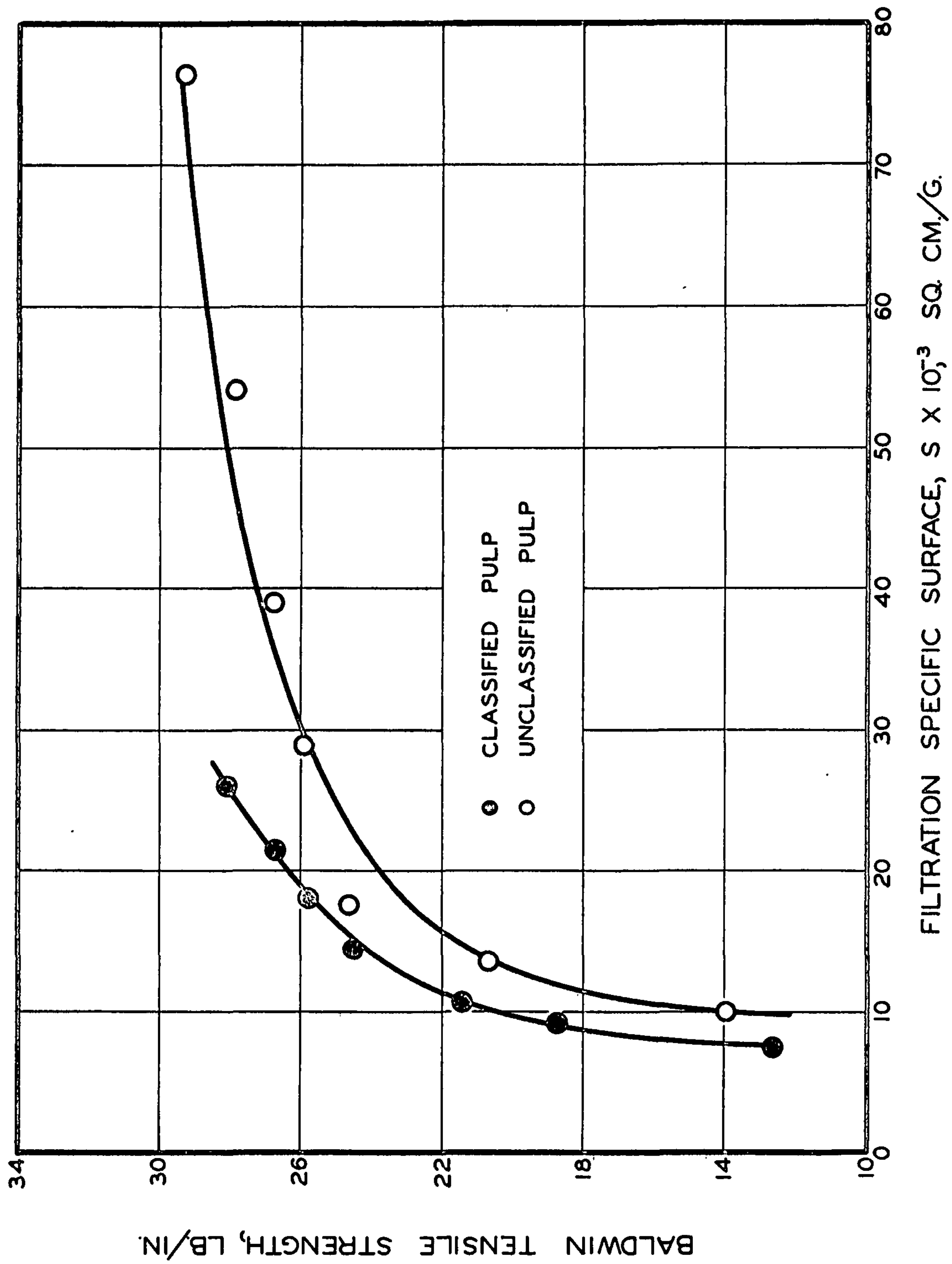

Figure 19

Tensile Strength as a Function of Filtration Specific Surface

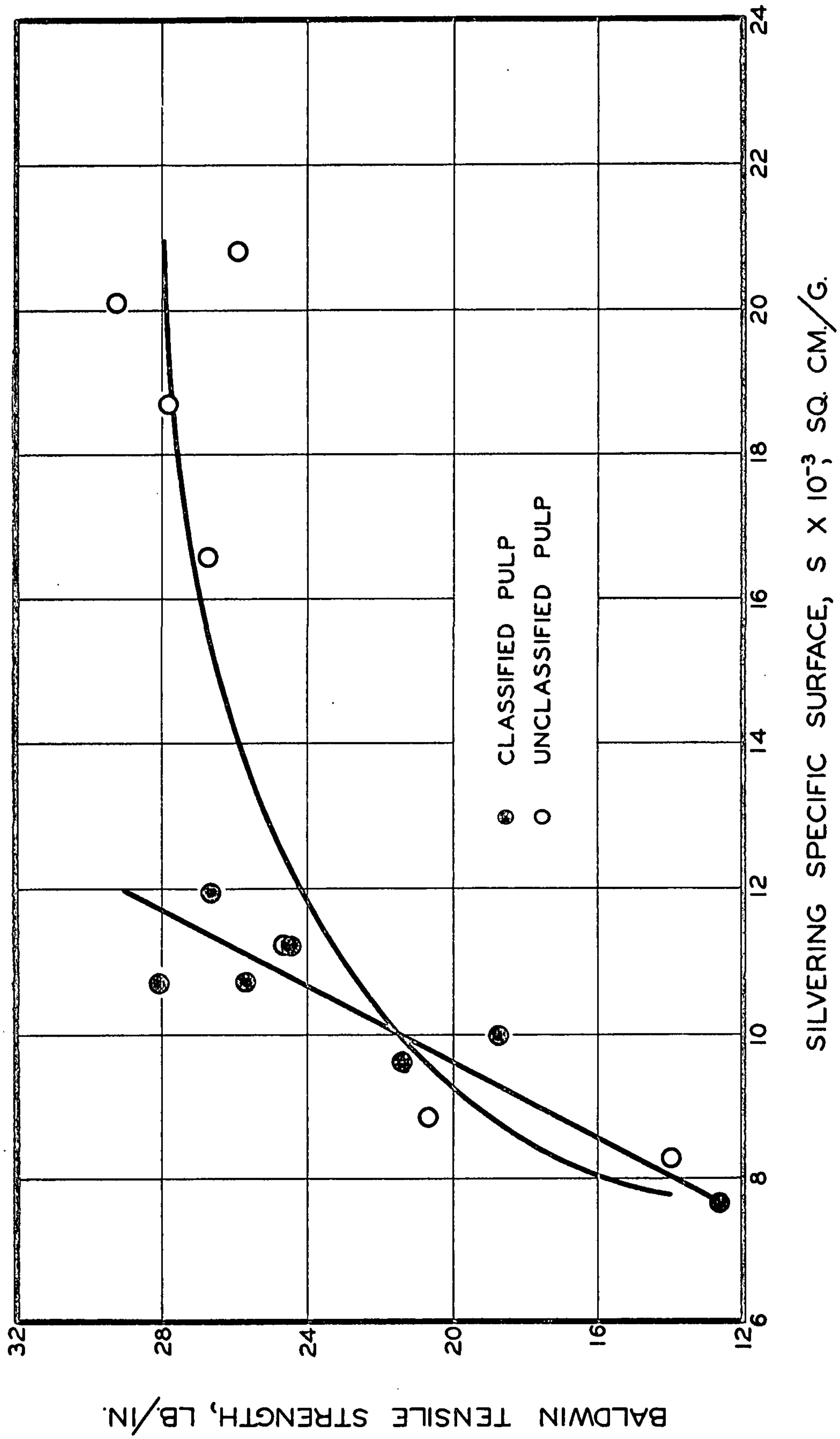

Figure 20

Tensile Strength as a Function of Silvering Specific Surface

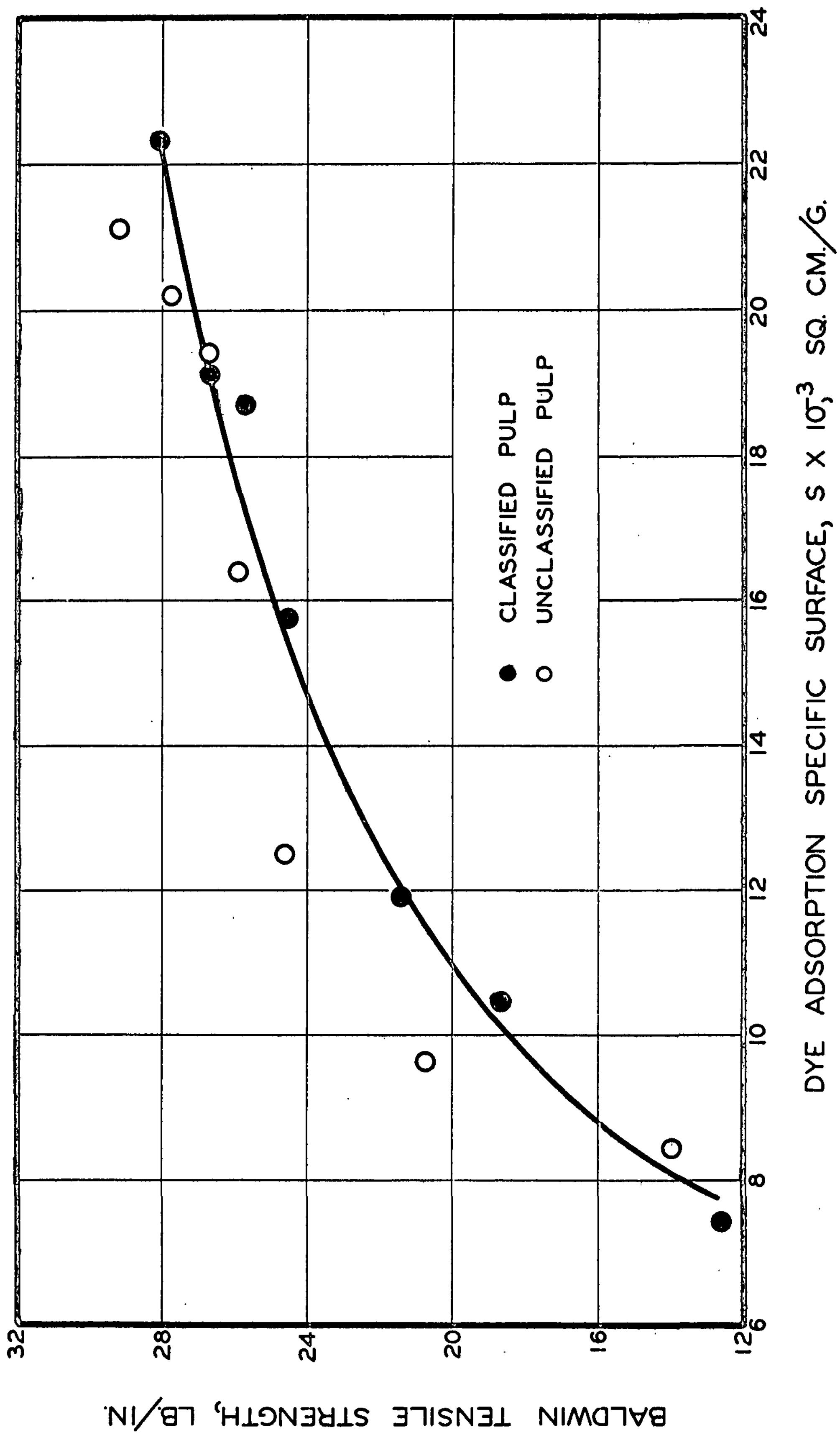

Figure 21
Tensile Strength as a Function of Dye Adsorption Specific Surface

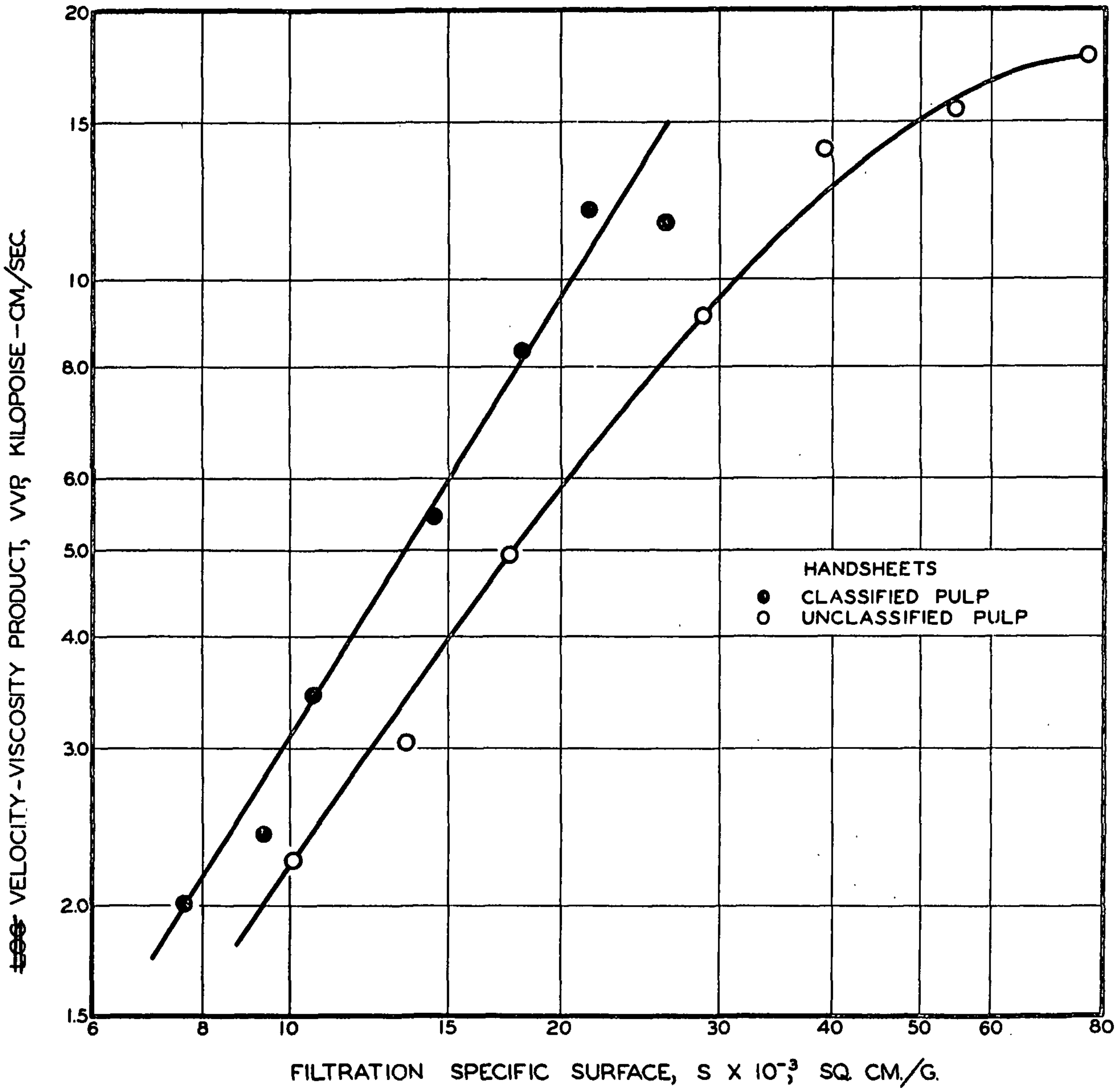

Figure 22

Velocity-viscosity Product as a Function of Filtration Specific Surface

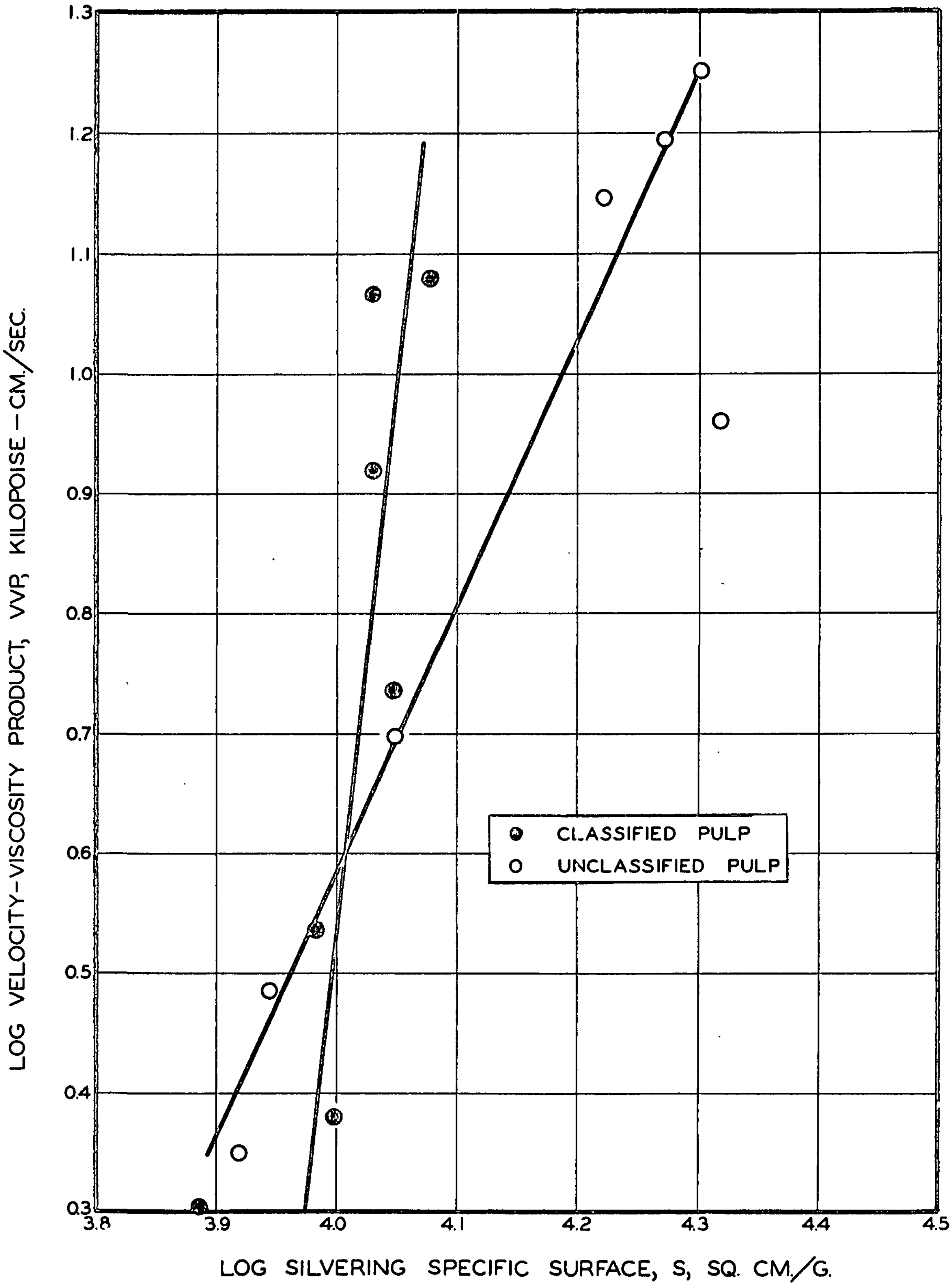

Figure 23

Velocity-viscosity Product as a Function of Silvering Specific Surface

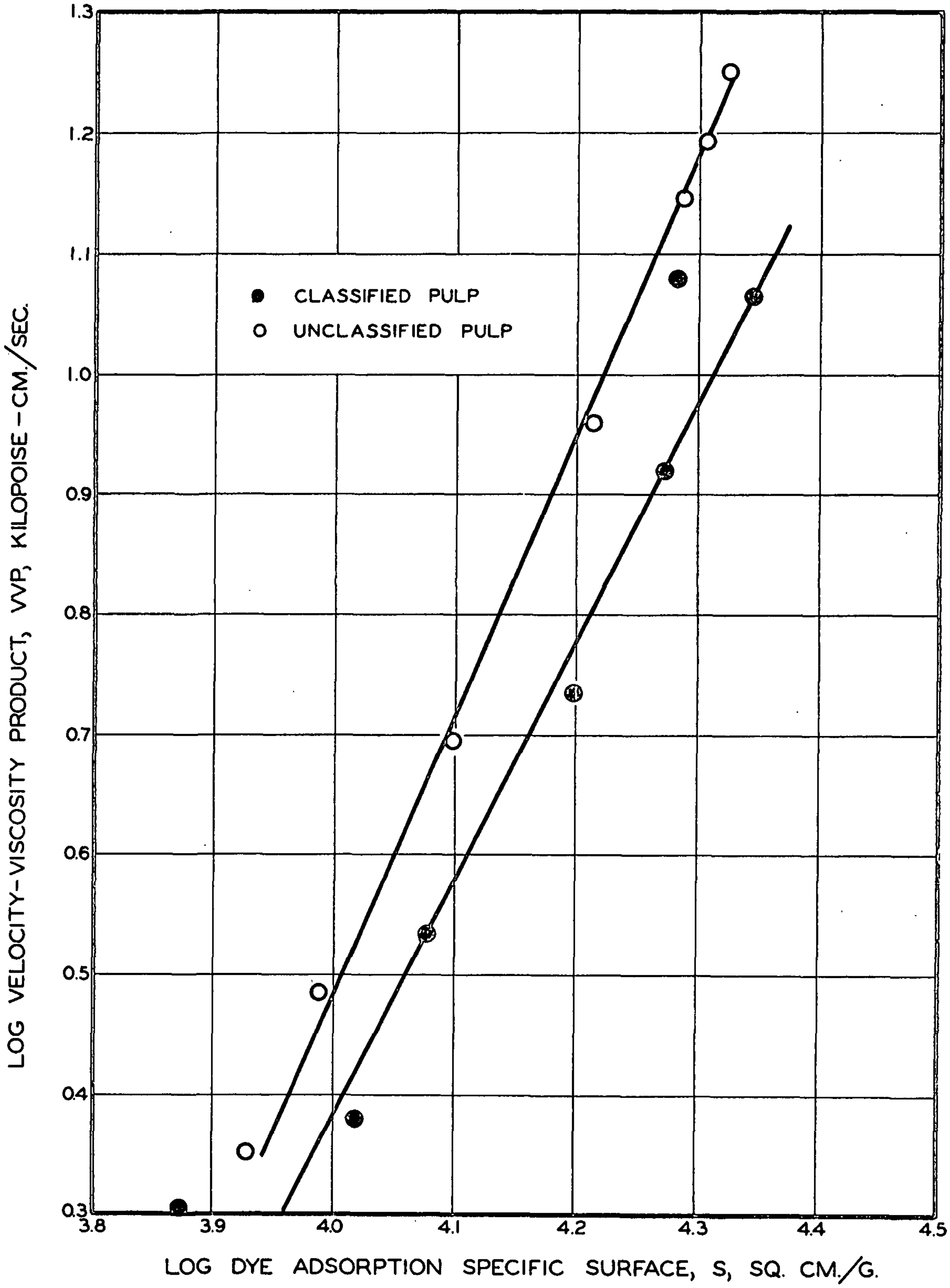

Figure 24
Velocity-viscosity Product as a Function of Dye Adsorption Specific Surface

strength properties against surface area, the parameter being whether the pulp is classified or unclassified. This comment applies to all cases except tensile strength versus dye adsorption because the above parameter has no influence in that case and the data have been treated as the same for both classified and unclassified pulp.

The relationship of the various surface area values with beating time and of the various strength properties with beating time have been previously discussed. It may appear that the correlation of strength properties with surface area reflects but the fact that both are changed with time of beating. A comparison with the freeness test, however, should indicate the presumably greater basic significance of a strength-surface area correlation than, say, a strength-freeness correlation. Attention is first called to Figure 25 showing the change in freeness with beating time for both classified and unclassified pulp. This shows the extraordinarily large effect of fines on freeness. Note that because of fines removal there is very little change in freeness for the classified pulp over the entire beating range. If the tensile strength, for example, as in Figure 26 is plotted as a function of freeness, it may be seen that while a reasonable apparent correlation may be found for the unclassified pulp, no useful correlation exists for the classified pulp.

The freeness test was developed as a measure of "drainage rate" and of "beating degree," the latter quantity presumably being an indication of the extent of maceration or fibrillation of the stock in preparation for its role in forming a sheet of paper. As Clark has so

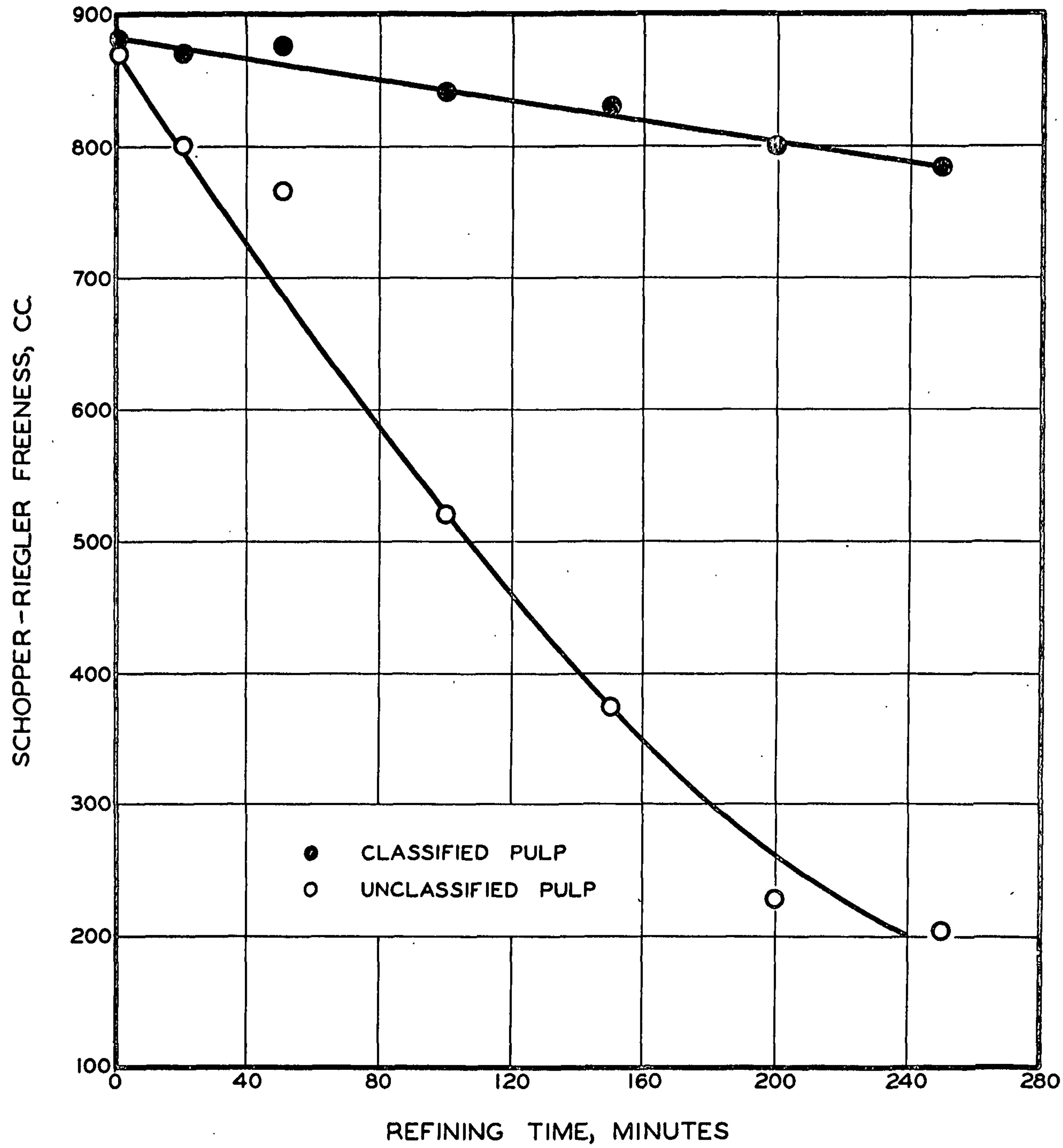

Figure 25

Freeness-Refining Time Relationship

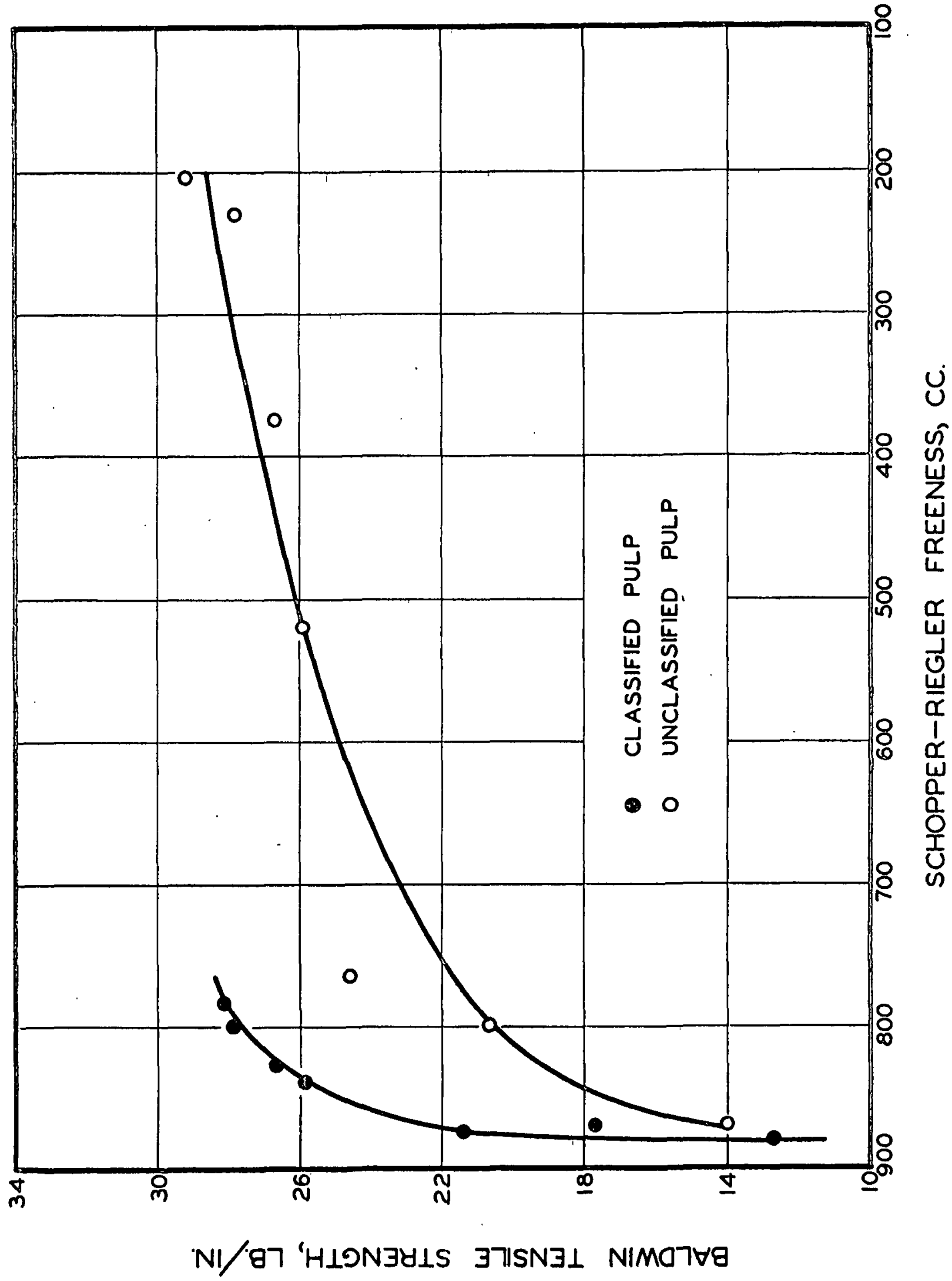

Figure 26

Tensile Strength-Freeness Relationship

aptly put it, it is a simple matter to "wash away hydration a la Schopper-Riegler" by removing fines (27). Since, as the present experiments have shown, fines removal (restoring freeness nearly to that of unbeaten stock) has but a small effect on some strength properties and a larger effect on others, it is obvious that a test dependent almost solely on fines is useless for pulp strength evaluation.

Determination of the external specific surface by filtration resistance is sensitive to fines but does not depend on fines. A good correlation between filtration surface area and tensile strength may be found for both unclassified and classified pulps, because the development of additional surface on the fiber brought about by beating is properly revealed by this method of external surface determination. Thus, a true, fundamental measure of beating degree, as defined above, is not the freeness test on any kind of stock but is the filtration resistance test on classified pulp. Also, since the more empirical dye adsorption method is insensitive to fines, dye adsorption estimation of beating degree has far greater validity than that based on freeness.

As will be explained in the section to follow, it is not necessarily believed that external specific surface, as such, is an essential physical criterion of pulp strength. It is believed that external specific surface is rather simply and directly related to those fundamental properties which bring about pulp strength and thus may be legitimately employed in a correlation. If the total, at least, of the external surface is one of the factors accounting for sheet strength, then the good correlation of strength properties with external surface may be considered a support of such relationship. The fact that fines removal produces only a change in slope in such relationship is encouraging in that direction. We may profitably examine certain specific physical tests and see if their relationship to external surface can throw light on its influence on physical properties.

Bonding strength, as determined by the velocity-viscosity product, shows a good correlation, as shown in Figures 22, 23, and 24. Although not illustrated here, a similar relationship may be shown between M.I.T. fold and external surface (see Figure 5, page 17, Progress Report Fifteen (13). Something of a drop-off is observed at the highest beater intervals, but the relationships are good straight lines over most of the range. Since these two tests are believed to be largely a function of interfiber friction or possibly interfiber adhesion, it is of interest to note that such test results appear to increase as something of a power function of external specific surface.

If comparison is made of the tensile-surface area correlation obtained in this investigation with some of those previously reported by such workers as Corte (28) and Thode, Beamesderfer, and Chase (29), some differences in the shape of the curves will be noted. It is thought that these differences are largely the result of the different beating actions in a ball mill and beater. The change in fiber length distribution, the varying ratios of bruised fibers to cut fibers, and the different ratios of discrete fiber fines to gelatinous debris all would modify the relationship in question. The results here presented are thought to be valid for the case of ball mill beating, where fiber-length distribution is but slightly altered by beating and where fine fibers in the fines fraction are at a minimum.

G. APPLICATION OF SURFACE AREA DATA

One limitation with which we are always faced in interpreting results of a single beater experiment is that the similarity of trends of all the various properties is such that virtually anything will correlate with anything else. The question immediately arises in any attempt at pulp evaluation as to what happens to the various relationships contemplated when comparing pulps, one with another. The ultimate aim of any pulp evaluation program must be the determination or preferably prediction of properties of a new and unknown pulp on the basis of more or less rigorous physical and chemical tests, and such determinations must be made in comparison with pulp or products of known properties.

In a recent article, Thode and Gorham (30) suggested that two fundamental variables relating to pulp which might serve to characterize strength properties in handsheets would be the external specific surface and the cupriethylenediamine viscosity of the pulp. In making that suggestion, it was not presumed that these properties were the only ones of major importance but it was assumed that within a given type of pulp, such as sulfite pulp, the area available for bonding and the inherent strength of the fibers (as predicted by the degree of polymerization of the fibers) would be the most important factors. A multiple correlation analysis presented in the paper referred to did show a good correspondence of tensile strength with external specific surface and cupriethylenediamine viscosities of a number of sulfite pulps from different sources. There was still considerable scatter to the data indicating that other variables intervened, and there was considerable doubt that the validity of the treatment could extend to extraordinarily different wood species or extraordinarily different pulping processes, such as alkaline processes.

The above suggestion does provide, however, at least a beginning on the matter of prediction of pulp comparison. Perhaps not external specific surface area, as such, but bonded area is more to the point. Perhaps not the D.P. of the cellulose, but the individual fiber strength of the wood pulp is more to the point. Perhaps such factors as fiber length distribution must be included. It does appear, however, that from our studies of the beater processing of a single pulp a better understanding is evolving of the interrelationship of pulp properties so that future work on the comparison of pulp may be oriented toward the studies of factors whose importance is known and appreciated.

Certainly the full importance of the external specific surface to pulp strength properties will not be fully appreciated until comparisons of various pulps are available. The present work has served a very great function in delimiting for the first time the exact comparisons between the filtration resistance, dye adsorption, silvering, and optical methods of surface area determinations, all on the same pulp. Now we may build on such observations in making important comparisons of pulps in the future.

VI. BONDED AREA

A. SUMMARY

An optical technique was used to measure specific scattering coefficients of handsheets, and the data were utilized in estimates of relative bonded area. By correlating tensile strength with the bonded area indicated from the scattering coefficient data, it appeared that the total dry area available for fiber bonding, which is effective in developing tensile strength, remains constant with refining time, and is unaffected by the production of fines or the degree of fibrillation. When solvent-drying is used to prepare unbonded handsheets to estimate the total area available for fiber bonding, spuriously high values of relative bonded area are obtained for the following reasons:

(1) Solvent-dried fibers undergo relatively little shrinkage and therefore the swollen external area and lumen area contribute to light scattering.

(2) When beaten, a part of the exposed fibrils contribute to light scattering. These fibrils do not represent the full extent of external fibrillation as measured by a filtration technique, but rather correspond very roughly to the surface area measured in the silvering method.

In estimating the total area available for fiber bonding, the area required is the total dry fiber area. Apparently, this area is lower than indicated for solvent-dried fibers because of fiber shrinkage, bonding of fibrils to parent fibers, and bonding of part of the lumen surface. A further complication for solvent-dried fibers

is caused by the presence of a variable amount of fines in whole pulps. The fines affect the specific scattering coefficient but do not contribute to the effective bonded area.

It is recommended that solvent-dried handsheets should not be used to estimate relative bonded area. The best present method for determining the total dry fiber area available for bonding consists of extrapolating the specific scattering coefficient and tensile strength relationship for an unbeaten pulp at relatively low degrees of wet-pressing to zero tensile strength. The assumption is made that the specific scattering coefficient, s, is proportional to fiber specific surface, and the difference between the extrapolated s value and subsequent s values for water-dried handsheets is taken as proportional to the effective bonded area. This difference, divided by the extrapolated s value, is the relative bonded area which is effective in developing tensile and other related strength properties.

The data were used to estimate the absolute values of bonded area, and it was assumed, as found by Haselton (19), that a linear relationship exists between specific scattering coefficient and the fiber area determined by nitrogen gas adsorption. For the classified pulp with fines removed, the total dry fiber measured by light scattering was 9400 sq. cm. per g. Of this total area, 6850 sq. cm. per g. (73%) was external surface area and 2550 (27%) was unbonded lumen surface. It was estimated that the total dry lumen surface was about 4450 sq. cm. per g., and in drying these unbeaten fibers from water about 57% of the lumen surface is bonded. Relative bonded areas, calculated from optical data, are dependent upon the amounts of external and internal bonding. If the assumption is made that the lumen surfaces available for bonding are bonded to the same extent as the external surface areas, the correlation between s and nitrogen adsorption area may be used to translate relative bonded area into absolute values of external bonded area.

The predicted linear relationship between specific scattering coefficient and nitrogen adsorption area for the pulp in these studies differed significantly from Haselton's correlation for a similar pulp. There is evidence indicating that the nature of the correlation depends upon the relative amounts of internal and external areas for the fibers under consideration, and the observed differences are attributed to this fact.

It was argued that the beaten pulps in this study had little or no change in bonding strength and stress distribution because of refining. Hence, at the same total effective bonded area the pulps should have the same tensile strength. This was found to be true for classified pulps with no fines present and unclassified whole pulps with appreciable quantities of fines at various degrees of wet-pressing and beating. The validity and utility of the concept of total dry fiber area available for bonding being independent of beating was supported by these data.

B. INTRODUCTION

It is recognized that one of the important factors that affect paper strength is the amount of interfiber bonding that exists in a sheet of paper. The most widely used method for estimating the amount of bonded area in paper is the so-called optical technique that was originally studied by Parsons (31), and later explored by Ratliff (32). The technique was utilized by Keeney (33) and Leech (34) in their studies of paper strength. The latest and most significant contribution to our understanding of the method was made by Haselton (18, 19) who combined optical measurements with studies of gas adsorption determinations of the amounts of unbonded and bonded area in paper. The results of these workers have indicated the utility of the method and have supported some of the principles of the optical technique for studying bonded area. However, evidence has also been presented that shows significant differences in the various methods for obtaining either optical data or area measurements for the total area of dry and unbonded fibers. Some of the observations made by the above investigators have been used as a framework to design a program for further investigation of bonded area in the integrated studies, and this section of the report presents the results of this phase of the work.

Ratliff (32) and Haselton (19) have discussed the optical method in some detail and recently Swanson (35) has reviewed the literature related to fiber bonding. Thus, only some of the more critical assumptions and important principles will be summarized here.

The optical method utilizes numerical values of the specific scattering coefficient which may be calculated from the original theory of Kubelka and Munk (36, 37). This theory quantitatively relates the scattering and absorption of light to the diffuse reflectance of a light scattering medium. The most convenient form of the theory as adapted specifically to paper has been presented in equations and charts by Steele (38) and Judd (39). Van den Akker's (40) suggestion that specific scattering coefficient and specific absorption coefficient be redefined in the more useful manner of a basis weight (in c.g.s. units) instead of a thickness basis has been generally followed by workers in the paper field.

By measuring two diffuse reflectances, R_o, the reflectance of a single sheet backed by a black cavity, and R_∞, the reflectance of a sheet backed by a thick pad of the same material, the scattering power, sW, may be read directly from charts. Knowledge of the basis weight of the specimen, W, permits calculation of the specific scattering coefficient, s. Since the specific scattering coefficient is a function of the wavelength of light, the reflectances are measured for monochromatic light. In this study the General Electric Recording Spectrophotometer (GERS) was used.

The specific scattering coefficient, s, depends upon the size and shape of the particles in the light path and upon the difference between the index of refraction of the particle and the surrounding medium. In general, s increases with decreasing particle size until the particle size approaches a small fraction of the wavelength of the incident light; thereafter s decreases with continued decrease in particle size down to molecular dimensions. It is the dependency of s on the interfacial area between substances of different indices of refraction, i.e., fibers and air that is utilized in the optical technique for estimating bonded area. The simplifying assumption is made that s is directly proportional to the fiber specific surface, S, (expressed on an area per unit mass basis). Thus

$$s = aS \tag{1}$$

where $\underline{a}$ is a dimensionless proportionality constant. When $\underline{s}$ is measured for a water-dried handsheet, it is reasoned that the area involved in fiber bonding does not scatter light, and thus $\underline{s}$ is a measure of the unbonded fiber specific surface, $\underline{S}_u$, and specifically,

$$s_u = aS_u \tag{1a}$$

Ratliff (32) has discussed the relative distances of separation of fiber surfaces that are involved in establishing fiber bonds and in creating surfaces in complete optical contact. It is known that the forces responsible for the bonding of fibers, such as hydrogen bonds and other Van der Waals forces, are effective only over distances of several Angstrom units (A.) whereas complete optical contact (where no light is scattered) involves distances of a small fraction of the wavelength of the incident light, i.e., approximately 400-500 A. It is probable that there is no sharp line of demarcation between the presence or absence of optical contact up to perhaps several multiples of the wavelength of the incidental light. However, Ratliff reasoned that if fiber surfaces were brought into proximities where optical interference could take place, the surface tension forces resulting from drying would ultimately lead to the bonding of these surfaces. It is possible, however, that the optically bonded area is greater than the true area involved in fiber bonding, and the approximate nature of Equation (1a) is emphasized.

To obtain a measure of the total available surface area for fiber bonding, $\underline{S}_t$, unbonded handsheets are formed by replacing water by acetone and then butanol (18). After drying, the specific scattering coefficient is determined, and Equation (1) for the totally unbonded fibers becomes

$$s_t = aS_t \tag{1c}$$

The relative bonded area ($\underline{S}_b/\underline{S}_t$) may now be estimated since the bonded area, $\underline{S}_b$, equals the total area minus the unbonded area ($\underline{S}_t - \underline{S}_u$), and

$$\frac{S_b}{S_t} = \frac{s_t - s_u}{s_t} \tag{2}$$

Leech (34) and Haselton (19) have noted that the scattering coefficient for butanol-dried spruce sulfite fibers is higher than the $\underline{s}$ value for water-dried but unbonded fibers. Haselton argued that this would be expected since the butanol-dried fibers have undergone relatively little shrinkage during drying and would correspond more closely to fibers in a water-swollen condition. Haselton used a method equivalent to extrapolating a tensile strength (at various wet-pressings) and $\underline{s}$ relationship for unbeaten fibers to zero tensile strength to obtain a correct $\underline{s}$ value for water-dried and unbonded fibers. He proposed that subsequent butanol-dried $\underline{s}$ values be corrected by the same ratio of the extrapolated $\underline{s}$ to butanol $\underline{s}$ for the particular fibers in question. Since it is known that the degree of swelling of fibers is dependent upon the amount of beating (9, 41), this assumption of a constant correction factor for the butanol specific scattering coefficients may be in serious error. It was decided in the integrated studies to attempt to obtain extrapolated values for $\underline{s}$ at different refining intervals using a technique of relating $\underline{s}$ values to tensile strengths at a given beating time for various degrees of wet-pressing.

Haselton (19) obtained a remarkable correlation between s and the area of water-dried handsheets as measured by application of the Brunauer, Emmett, and Teller equation to nitrogen adsorption isotherms. The data were precise enough to extrapolate accurately to a small positive value for area at zero s. Haselton pointed out that at 100% bonded area ($S_u = 0$), light would still be scattered at the two surfaces of a paper specimen. He estimated this point for standard handsheets as being an area of 400 sq. cm. per g. at an s value of 12 sq. cm. per g. The relationship between s_u and S_u was linear for a bleached spruce sulfite pulp at various wet-pressing and beating intervals. Haselton noted that nitrogen adsorption probably does not take place on that area involved in fiber-to-fiber bonding and because of the relatively small diameter of a nitrogen molecule (4.3 A.), the water-dried fiber area measured by gas adsorption is very close to the actual unbonded area of a sheet of paper.

It was decided to determine the relationship between s_u and S_u for the pulps under investigation in the integrated study using a nitrogen adsorption technique. Although the original Haselton gas adsorption apparatus was used in the studies reported in Progress Report Fourteen on solvent-dried fibers (21), a new apparatus was constructed to give more precise data for the relatively low areas present in water-dried handsheets. These data are not complete and will be presented in a later report. However, several important implications of the Haselton correlation between s and nitrogen gas adsorption area will be discussed later in this section of the report.

To obtain absolute values of bonded area, the constant of

Equation (1) relating s to S must be established. Since Leech and Haselton have shown that differences may exist between the scattering coefficient of water-swollen and air-dried fibers, it is preferred that the correlation be made for fibers dried from water. In the past, many workers (31-34) have correlated the s values of butanol-dried fibers with specific surface of water-swollen fibers as measured by the silvering technique. Silvering data were obtained in this study for comparison with other area determinations.

C. EXPERIMENTAL PROCEDURES

Specific scattering coefficients were measured for the seven refining intervals of classified and unclassified pulps at various degrees of wet-pressing with the GERS and using reflectance values R_o and R_∞ at 650 millimicrons. At each refining interval, the water-formed handsheets were treated at seven wet-pressures of from essentially zero to about 150 p.s.i. and Schopper tensile strengths were measured. In addition, s values were measured for the standard wet-pressed handsheets at two additional wavelengths of 450 and 550 mμ. Unbonded handsheets were obtained by displacing the water with acetone and then butanol as outlined by Haselton (19), and s values were obtained for these solvent-dried fibers. The data are given in Tables V and VI.

D. RESULTS AND DISCUSSION--SCATTERING COEFFICIENT MEASUREMENTS

The specific scattering coefficients for the butanol-dried sheets and standard handsheets are related to refining time in Figure 27. The s values for the unbonded fibers dried from butanol increase linearly with refining time but show considerably more deviation from

TABLE V

SCATTERING COEFFICIENTS AND TENSILE STRENGTHS FOR BUTANOL AND WATER-DRIED SHEETS

Refining Time, min.	Pressing Load, lb./sq. in.	Schopper Tensile Strength lb./in.		Specific Scattering Coefficient,* sq. cm./g.	
		Unclassified	Classified	Unclassified	Classified
0	Butanol	--	--	429	400
	0	5.4	3.6	308	285
	1	6.7	4.6	309	302
	10	9.5	6.4	303	294
	25	10.6	7.7	292	280
	50	11.5	9.0	272	273
	150	14.7	12.3	232	238
	Standard	13.5	12.0	242	239
20	Butanol	--	--	488	426
	0	11.8	8.8	282	273
	1	12.2	11.2	272	262
	10	16.9	15.9	246	238
	25	17.7	15.6	232	239
	50	18.4	16.8	214	221
	150	22.2	20.9	169	184
	Standard	21.1	19.2	189	199
50	Butanol	--	--	539	466
	0	14.4	10.8	265	261
	1	15.9	12.0	248	246
	10	19.1	17.3	227	224
	25	20.2	16.9	208	218
	50	21.6	17.6	188	198
	150	22.9	18.3	142	158
	Standard	22.0	19.5	162	172
100	Butanol	--	--	596	501
	0	18.4	16.7	228	231
	1	18.2	18.2	199	206
	5	--	22.3	--	191
	10	21.7	23.3	157	169
	25	23.3	22.1	157	164
	50	24.0	23.5	134	146
	150	26.3	--	96	--
	Standard	25.1	23.9	119	128
150	Butanol	--	--	685	613
	0	23.1	18.8	160	216
	1	21.2	18.1	140	191
	5	24.6	21.7	106	173
	10	24.8	22.4	110	163
	25	26.1	23.4	95	142
	50	26.1	23.6	97	122
	Standard	27.4	24.4	74	111
200	Butanol	--	--	761	556
	0	23.6	18.3	99	202
	1	25.0	19.1	88	177
	5	26.7	21.7	79	163
	10	26.3	21.7	77	148
	25	27.5	24.2	70	127
	50	27.4	24.7	59	113
	Standard	26.9	25.9	56	91
250	Butanol	--	--	847	594
	0	23.5	19.8	73	185
	1	24.3	20.6	68	162
	5	26.5	22.9	63	141
	10	25.9	23.3	64	136
	25	26.7	24.1	59	113
	50	27.0	24.9	66	92
	Standard	25.5	26.6	56	78

* Measured at 650 millimicrons

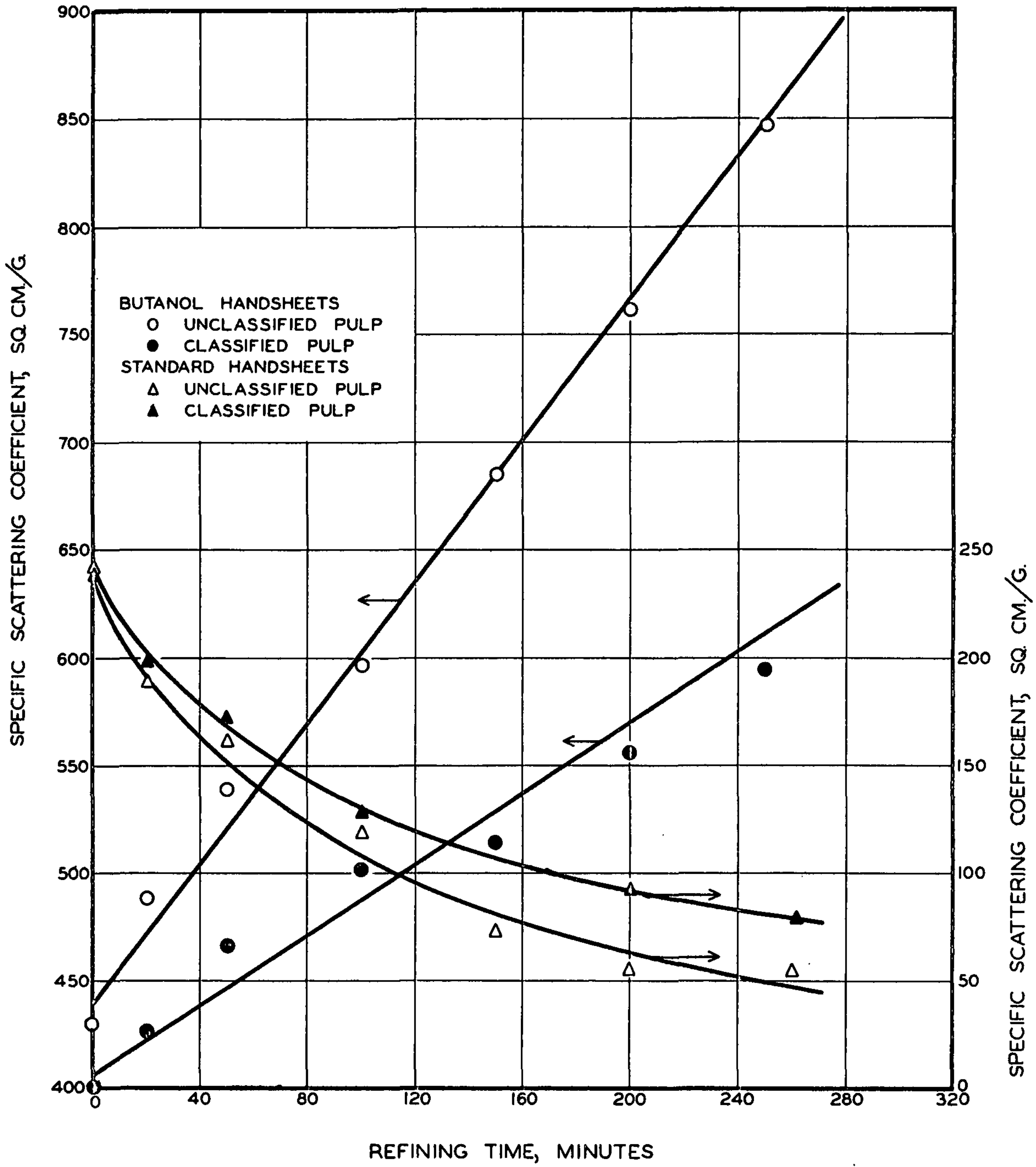

Figure 27

Specific Scattering Coefficients as a Function of Refining Time a given functional relationship than do the scattering data for the water-dried handsheets. Experimental difficulties in the formation of unbonded handsheets probably account for these deviations since it was qualitatively observed that some of the butanol-dried sheets had appreciable tensile strengths and therefore must have been bonded, in some cases, to an unknown and uncontrolled extent. It is possible that in some instances, evaporation of butanol from the handsheet could cool the surrounding air below its dewpoint and some condensation of water vapor may have occurred. Precautions were taken to prevent excess rates of evaporation but in the transfer of butanol-saturated sheets to a controlled environment some condensation may have taken place.

The relative rate of increase of s for butanol-dried fibers with refining time is about double for the unclassified pulp as compared to the classified pulp. This corresponds to the ratio of the initial rate of increase in filtration specific surface of unclassified handsheet stock to classified stock. However, it was noted in Progress Report Thirteen (9) that the rate of change of filtration specific surface of the unclassified handsheet stock with respect to refining time, increased with increasing refining time as the retention of fines became greater, and at high degrees of refining approached the specific surface of the whole, unclassified pulp. It is probable that, in the process of displacing water in handsheets with acetone and butanol, a highly beaten pulp will lose a significant amount of fines, and thus, the level of scattering coefficient values will depend markedly on this unknown and uncontrolled loss. Since Figure 27 clearly demonstrates the strong influence of fines on scattering coefficient, the significance of s values for any unclassified pulp is very doubtful.

The correlation between specific scattering coefficient of butanol-dried fibers and the silvering area of the fibers is shown in Figure 28. The scatter of the data is considerable and is caused mostly by inconsistencies in the silvering areas. However, the linear correlation shown is about as good a fit as those shown by Ratliff (32) and Keeney (33). It has been noted in Progress Report Thirteen (9) that there is no significant difference between the external surface area of the whole and handsheet classified pulp as measured by the filtration technique. This would be anticipated since fines are removed and there can be no area change because of fines loss in the formation of handsheets. However, Figure 28 shows that the greatest difference between silvering areas at a given s value is between whole and handsheet stock of the classified pulps. Corresponding values of area for the unclassified pulps generally lie intermediate between the whole and handsheet classified stock. Therefore, the data do not justify fitting more than one curve to the points. Similar scattering of silvering data have been noted by Keeney (33) to be dependent upon the presence or absence of fines. It may be concluded that the increase in s for butanol-dried fibers roughly correlates with the increase in silvering area, and the function can be approximated by a linear relationship as given by Equation (1).

In Figure 29 the specific scattering coefficient for classified butanol-dried fibers is correlated with the filtration specific surface. It is felt that the filtration technique gave the closest measure of the actual increase in area because of extensive fibrillation upon refining, and supposedly these fibrils will be available for light scattering in the butanol-dried handsheets. Since both s and the area

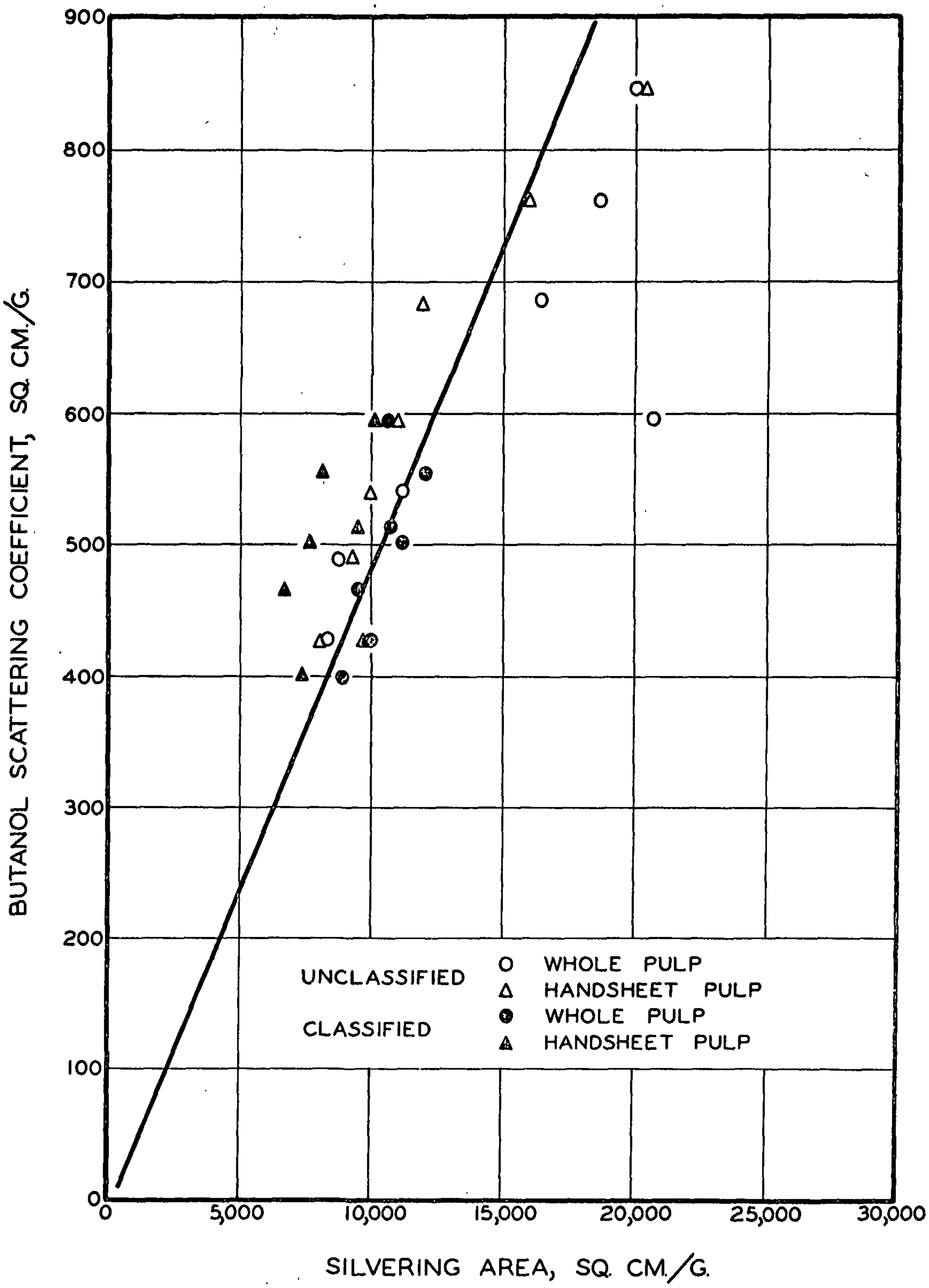

Figure 28

Specific Scattering Coefficient for Butanol Handsheets as a Function of Silvering Specific Surface

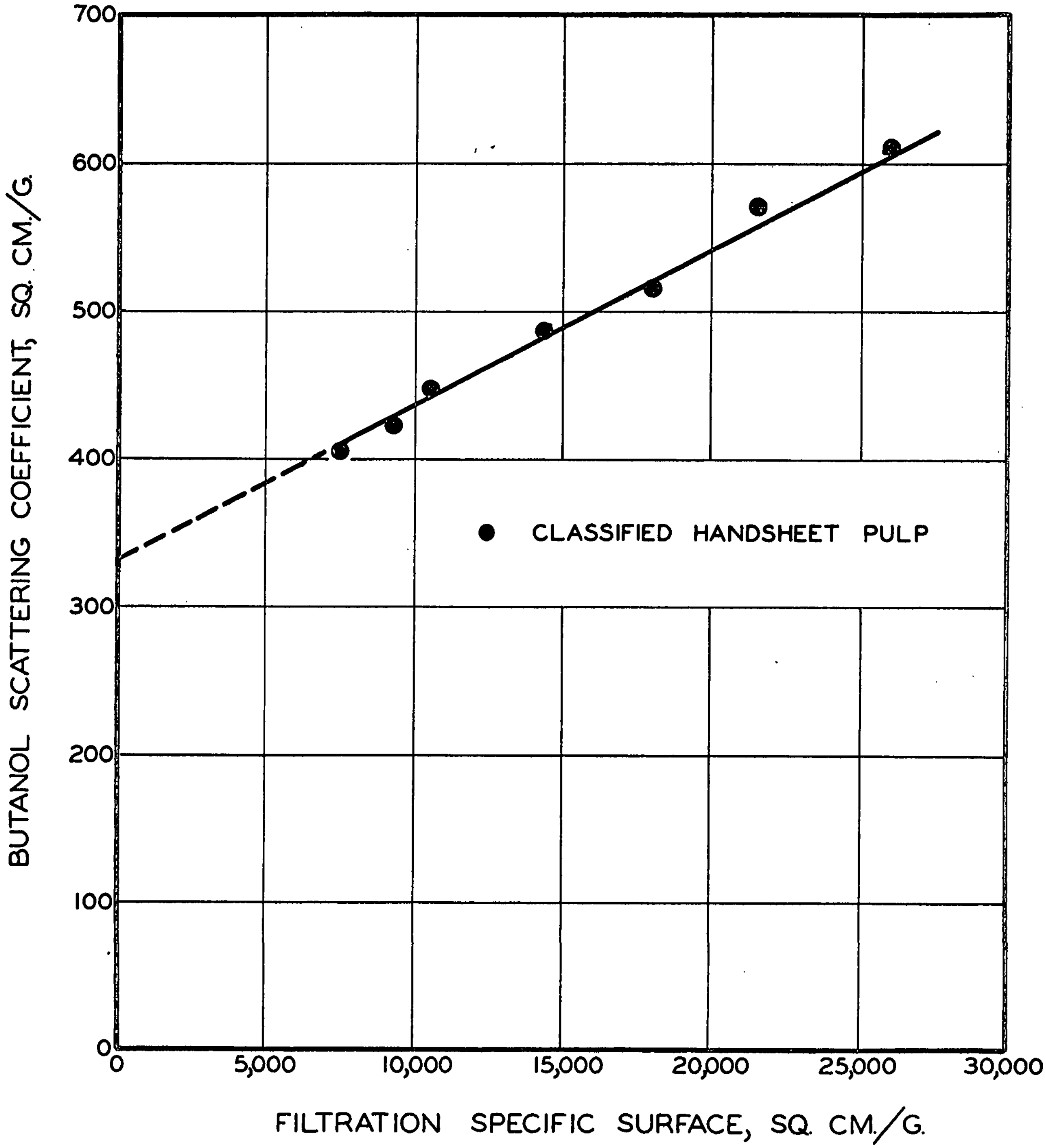

Figure 29

Specific Scattering Coefficient for Butanol Handsheets
as a Function of Filtration Specific Surface

under consideration were linear functions of refining time, they will of course give a linear relationship when correlated together. However, the curve extrapolates to a large positive value of s for zero area. An intercept might be expected, since the butanol-dried fibers have undergone relatively little shrinkage and were known to have a large internal area as measured by nitrogen adsorption (19). Although most of this large internal area will not scatter light because of small distances of separation, at the very minimum it would be expected that the lumen area of the fiber and perhaps some of the largest pores would scatter light. Then, if it is assumed that the fiber specific surface of Equation (1) is composed of external area, S_e, measured by the filtration technique, and some unknown, but constant, internal area, S_i, then Equation (1) may be written as

$$s = a(S_e + S_i) \qquad (1d)$$

and the internal area, S_i, may be estimated from the zero external area, S_e, intercept of Figure 29. This apparent internal area is about 32,000 sq. cm. per g. The unbeaten external fiber area is known to be 7,600 sq. cm. per g., and it can be estimated from the fiber cross-section data that the lumen area is about 65% of the external area, or about 5,000 sq. cm. per g. Thus, it may be estimated that the internal pore area, which is apparently scattering light, is about 27,000 sq. cm. per g. Since the total internal pore area of similar unbeaten butanol-dried fibers as measured by gas adsorption is about 29,000 sq. cm. per g. (19), it would not be likely for almost all this internal pore area to be separated by sufficient distances (0.6 A.) to create optical interference and thus contribute to the specific scattering coefficient. Haselton's data and other considerations support this evidence that internal fiber pore area does not contribute appreciably to light scattering. Haselton's correlation between specific scattering coefficient and nitrogen adsorption area for water-dried bleached spruce sulfite fibers is reproduced in Figure 30. The slope, or a value from Equation (1), for this line is 0.046 whereas the slope from Figure 29 and Equation (1d) is 0.015. This threefold difference in relationships between s and area for similar fibers must be false and it is hypothesized that the butanol-dried fibers are in a condition such that specific scattering coefficient does not characterize the true and full extent of fibrillation. Thus, the correlation between s and filtration specific surface is fundamentally unsound and any apparent relationship between these two variables is probably accidental.

To estimate relative bonded area, it is necessary to obtain a reliable measure of specific scattering coefficient (s_t) for water-dried but unbonded fibers for use in Equation (2). It was planned to extrapolate tensile strength as a function of s for various degrees of wet-pressing to zero-tensile strength, and it was anticipated that the data for each refining interval would extrapolate to increasingly higher s values, indicating an increase in total area available for bonding, S_t. However, examination of the data from Table V showed the relationship between s and tensile strength to be independent of the degree of beating, and the data for various degrees of wet-pressings at all refining intervals fell on one common curve as shown in Figures 31 and 32 for classified and unclassified pulps. The deviation of the points from the given functional relationship was considered to be caused mainly by the nature of the tensile test in which failure is always at the weakest point and localized basis weight or formation variations

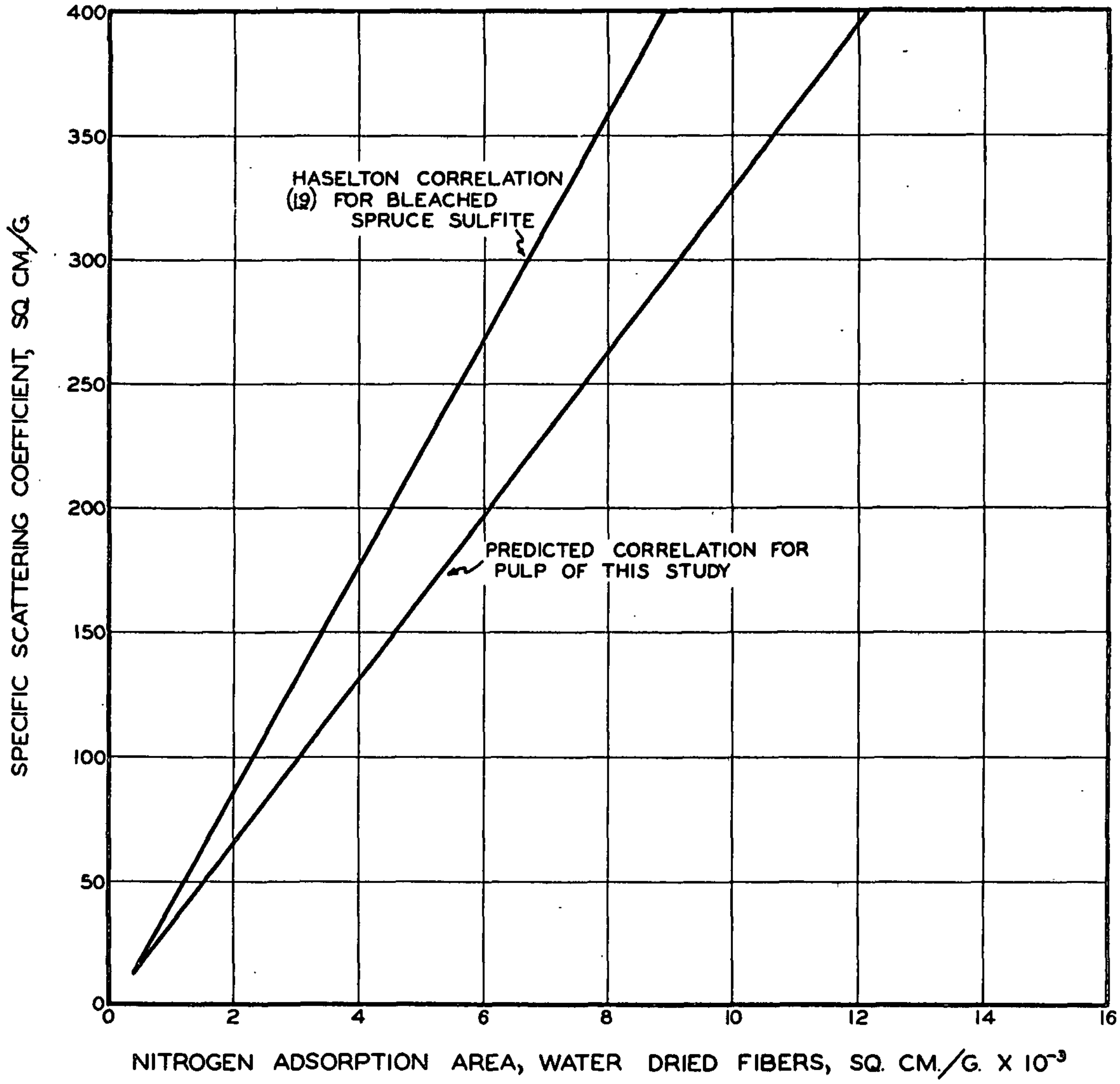

Figure 30

Relationship Between Nitrogen Adsorption Area and Scattering Coefficient

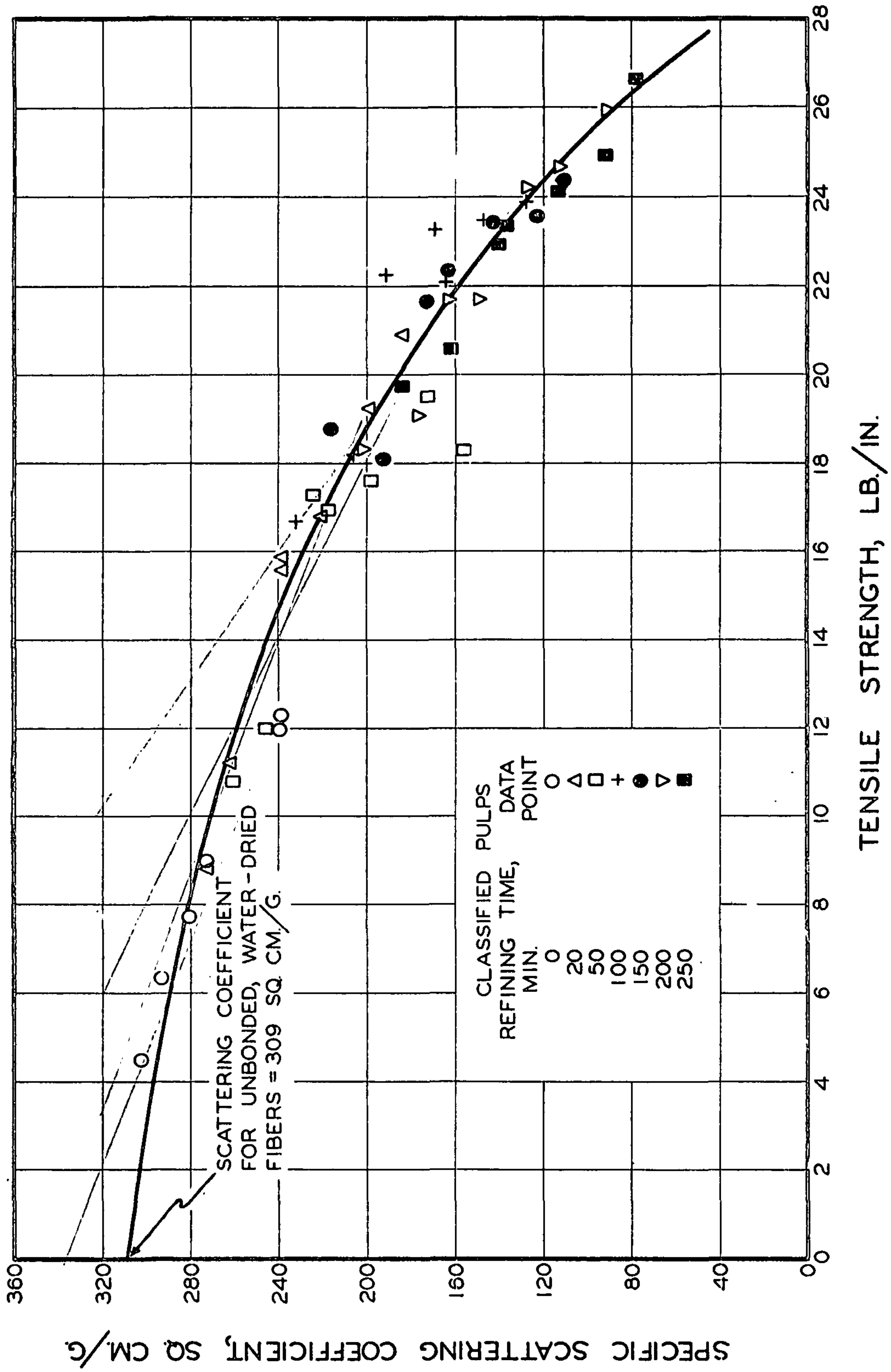

Figure 31

Scattering Coefficient-Tensile Strength Relationship at Various Wet-Pressing and Refining Intervals for Classified Pulps

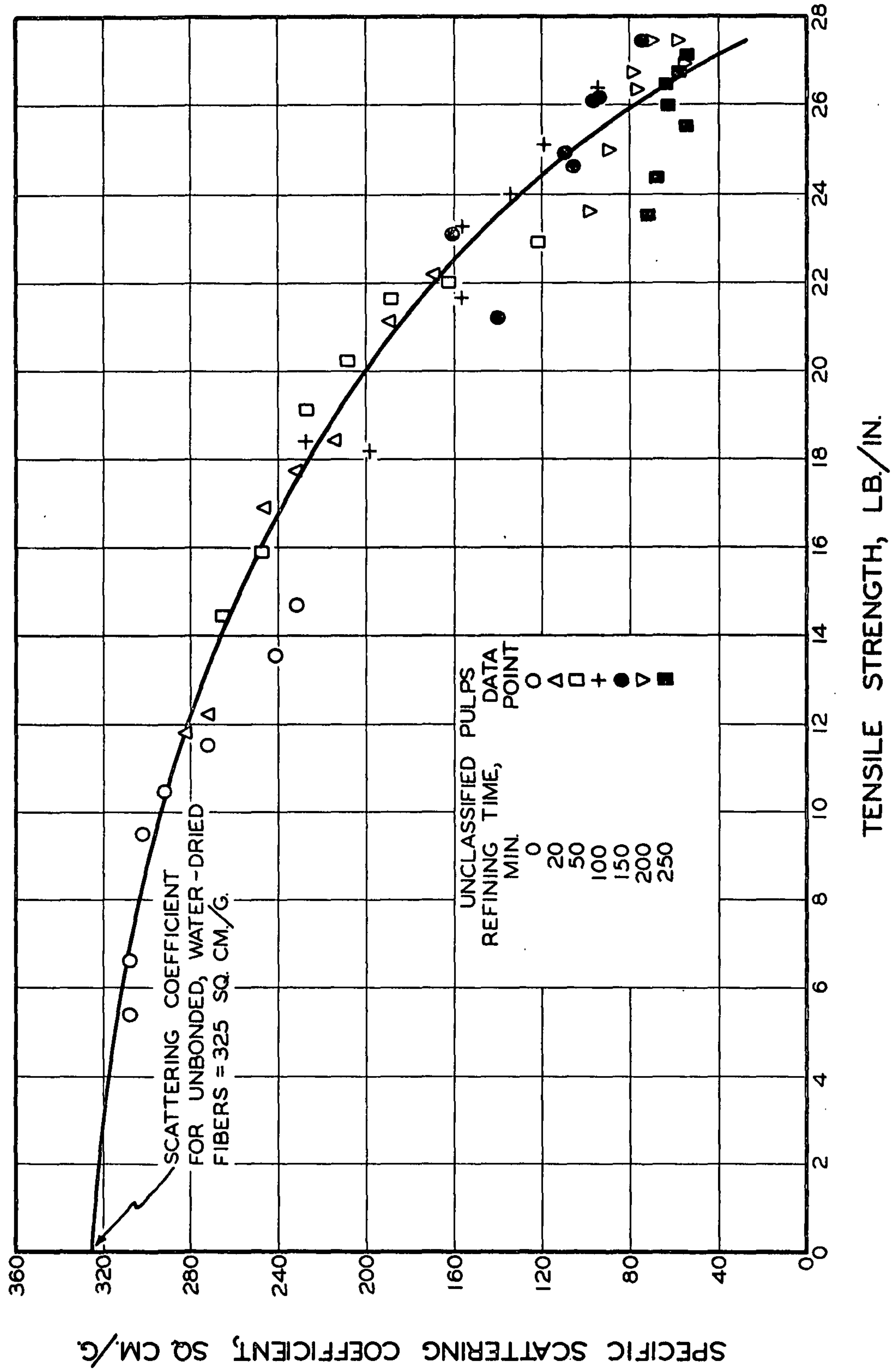

Figure 32

Scattering Coefficient-Tensile Strength Relationship at Various Wet-pressing and Refining Intervals for Unclassified Pulp may cause variation in the tensile strength values.[1]

The extrapolated values for s for dry, but unbonded, fibers were 309 and 325 sq. cm./g. for classified and unclassified pulps which correspond to values of s for butanol-dried and unbeaten fibers of 405 and 438, respectively (from Figures 31 and 32). Thus, the ratio of extrapolated s values to butanol s values was about 0.75 as compared to Haselton's (19) value of 0.68 for similar unbeaten fibers. Obviously, the butanol-dried fibers indicate a larger area than shown for the fiber dried from water. Since these ratios are for unbeaten fibers which do not have a fibrillated surface, it is probable that the greater area indicated for the butanol-dried fibers was contributed by the swollen state of the fibers and by the area of the lumen. Maximum and minimum values may be estimated for the ratio of s of water-dried to butanol-dried fibers by the following analysis:

For the classified, unbeaten pulp, microscopic, silvering, and filtration techniques all gave essentially the same value of 7600 sq. cm. per g. external surface area of the fibers in the water-swollen state. Microscopic measurements of equivalent fiber widths for the same pulp in the wet and dry states of 35.8 and 32.3 microns, respectively, may be used to estimate the effect of shrinkage on specific surface by assuming the surface area to be directly proportional to the equivalent fiber width. Also the microscopic measurements of relative external surface area and lumen surface area may be used to estimate

[1] A possible exception is the data for the 200 and 250-minute interval refining time of the unclassified pulp. These data show a high increase in tensile strength with relatively little decrease in scattering coefficient which is inconsistent with all the other data. Therefore, the accuracy of the tensile strength data for these two refining intervals is very questionable.

the lumen contribution (the ratio of swollen lumen perimeter to external surface perimeter was 0.65). Consider two extreme cases in which butanol-dried fibers have the complete swollen lumen surface and external surface available for light scattering wherein (1) the water-dried fiber has only the dry external surface available for light scattering, and (2) the water-dried fibers have both the dry lumen surface and dry external surface available for light scattering. In case (1), we would predict a ratio of s values of water-dried fibers to butanol-dried fibers of 0.55, and in case (2), an s ratio of 0.90 would be predicted. The experimentally observed value of 0.75 is intermediate between the two extremes. Because of its swollen state, the assumption that butanol-dried fibers have the complete lumen available for light scattering is probably good. However, it is probable that part of this lumen surface becomes bonded because of shrinkage during water drying and hence is unavailable for light scattering. Using the experimentally observed s ratio of 0.75, the amount of lumen area contributing to light scattering in water-dried fibers may be estimated to be 2550 sq. cm. per g. or about 57% of the total water-dried lumen area of 4450 sq. cm. per g. The water-dried fiber external area would be 7600 (32.3/35.8) or 6850 sq. cm. per g., and thus the total area giving an s value of 309 sq. cm. per g. is estimated to be (6850 + 2550) or 9400 sq. cm. per g. This total area would be that which would be measured by nitrogen adsorption, but until gas adsorption data are available, it must be recognized as merely an estimate from the presently available data.

A predicted relationship between specific scattering coefficient and nitrogen gas adsorption area for the pulp used in this study may be made on the basis of the above estimates. This predicted curve


1
2
3

Plate J
Classified Fibers 200 Minute Refining
Dry Fibers
150x


1
2
3

Plate K
Classified Fibers 200 Minute Refining
Wet Fibers
150x

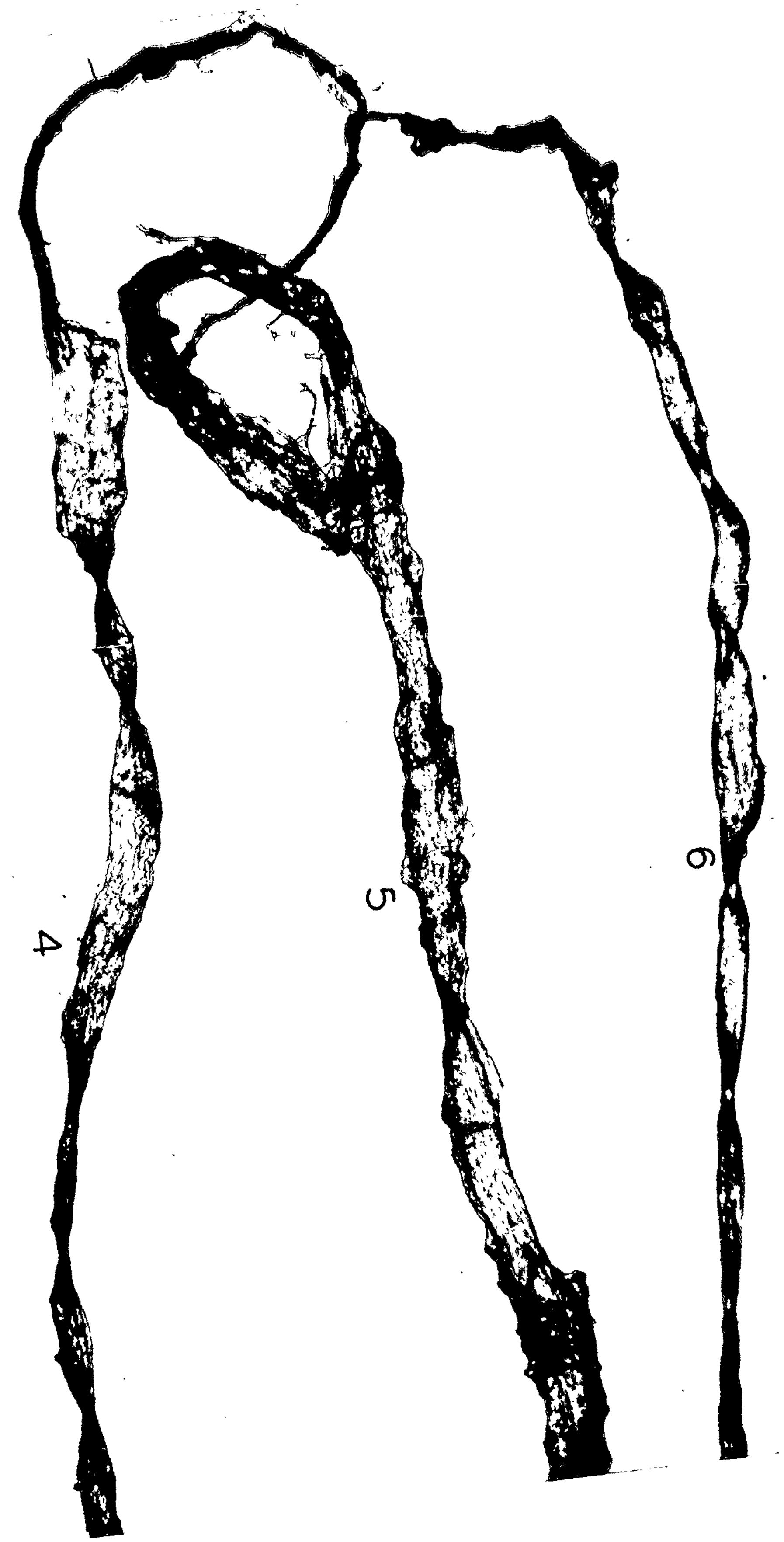
4
5
6

Plate L
Unclassified Fibers 200 Minute Refining
Dry Fibers
150x

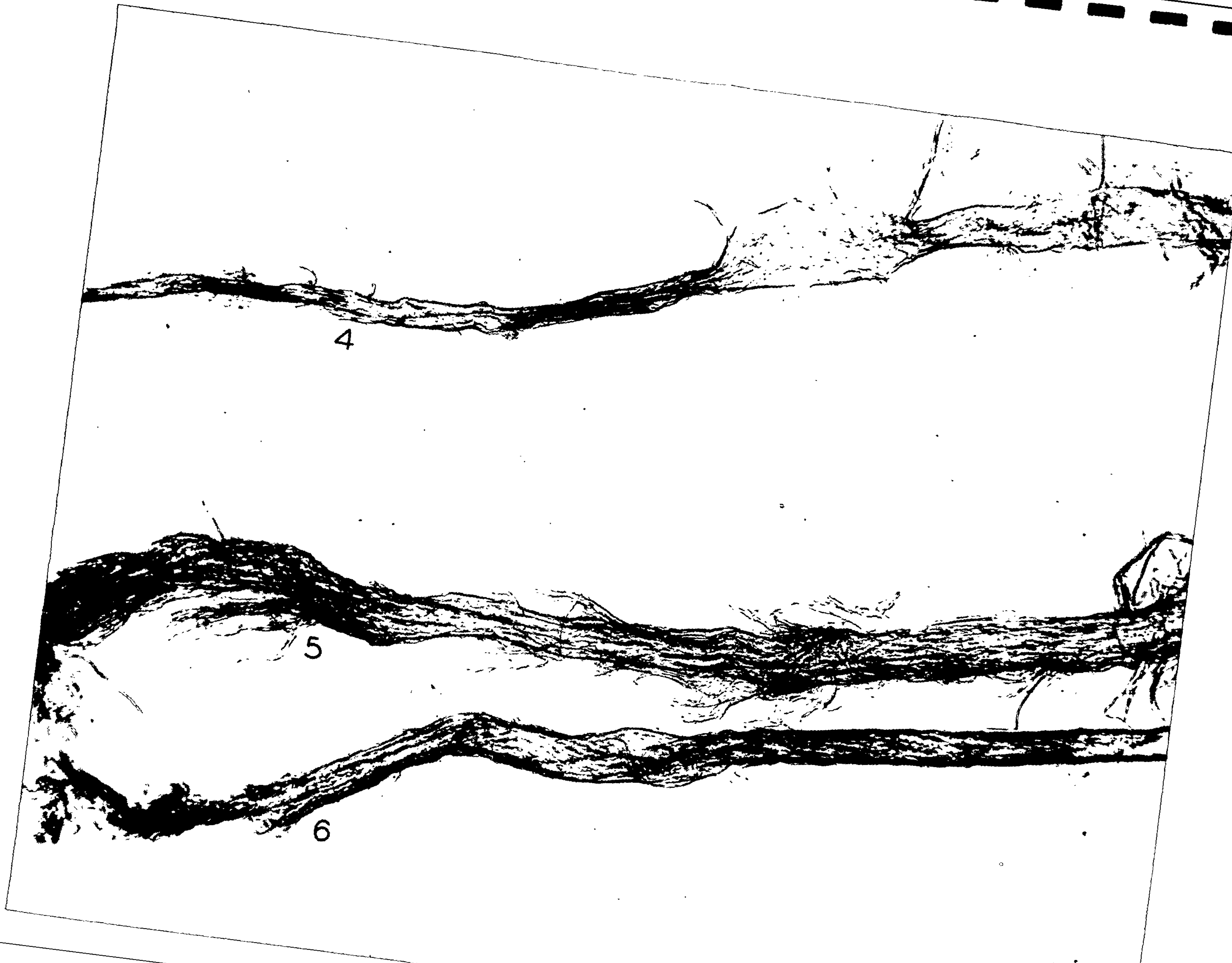
4
5
6

Plate M
Unclassified Fibers 200 Minute Refining
Wet Fibers
150x

has been compared to Haselton's correlation for his bleached spruce sulfite pulp in Figure 30 where a significant difference in the two relationships can be observed. It is doubtful that Haselton's correlation would apply to the pulp used in this study, since the extrapolated $\underline{s}$ value of 309 sq. cm. per g. for dry and unbonded fibers corresponds to an area of 6850 sq. cm. per g. as read from Haselton's curve. This is equal to the external surface area estimated for the dry, unbonded fibers of this study, and would indicate complete bonding of lumen surface. This is unlikely for unbeaten fibers and the actual correlation for the pulp under consideration here must have a somewhat smaller slope than found by Haselton for his fibers. Since the ratio of extrapolated and butanol-dried $\underline{s}$ values of Haselton's pulp was significantly lower than for the pulps in this study (0.68 as compared to 0.75), it is probable that differences in the relative amounts of internal and external scattering light is responsible for the difference in the two correlations.

One of the remarkable features of the correlations shown in Figures 31 and 32 is that the data indicate the total area of water-dried fibers, $\underline{S}_t$, remains constant and is independent of the degree of refining. The specific surface of the fibers in a water-swollen state is known to increase markedly with refining because of increased fiber swelling and extensive surface fibrillation. However, when dried from water, these fibrils probably bond back to the surfaces of parent fibers. This phenomenon is shown in Plates J, K, L, and M where photomicrographs of the same individual fibers in a wet and airdry state are given. It may be seen that the extensive fibrillation present in the wet fibers completely disappears in the dry fibers as the fibrils are rebonded to ?

the parent fibers. In the case of the unclassified pulp where large amounts of fines were known to be present, these fines have apparently bonded on the surfaces of parent fibers with the result that the total dry fiber surface remains essentially constant. Haselton (19) found that the nitrogen adsorption area of bleached spruce sulfite pulp which was spray-dried to prevent bonding stayed constant at a value of about 8000 sq. cm. per g. for Valley beater intervals representing a freeness decrease of from 860 to 750 cc. S.-R.

Assuming, as the data indicate, no increase in total dry fiber specific surface, $\underline{S}_t$, a number proportional to the bonded fiber surface, $\underline{S}_b$, may be estimated by

$$aS_b = a(S_t - S_u) = s_t - s_u \qquad (3)$$

The tensile strength data for various degrees of wet-pressing at different refining intervals are correlated with the product of the proportionality constant, $\underline{a}$, and bonded area, $\underline{S}_b$, as given by Equation (3) in Figures 33 and 34 for classified and unclassified pulps, respectively. Constant values for $\underline{s}_t$ of 309 and 325 sq. cm. per g. as determined from Figures 31 and 32 were used in the calculations. The relationship between tensile strength and bonded area is exactly the same for both classified and unclassified pulps. As a matter of fact, the curve shown in Figure 34 for the unclassified pulp was traced from the curve of Figure 33 for classified pulp. These data lead to the important conclusion that at the same total bonded area, the tensile strength of the pulps are the same irrespective of degree of refining, the amount of fines, or the extent of wet-pressing. The implication is that other important factors affecting sheet strength such as individual fiber strength, strength of fiber bonds, formation, and distribution of stress

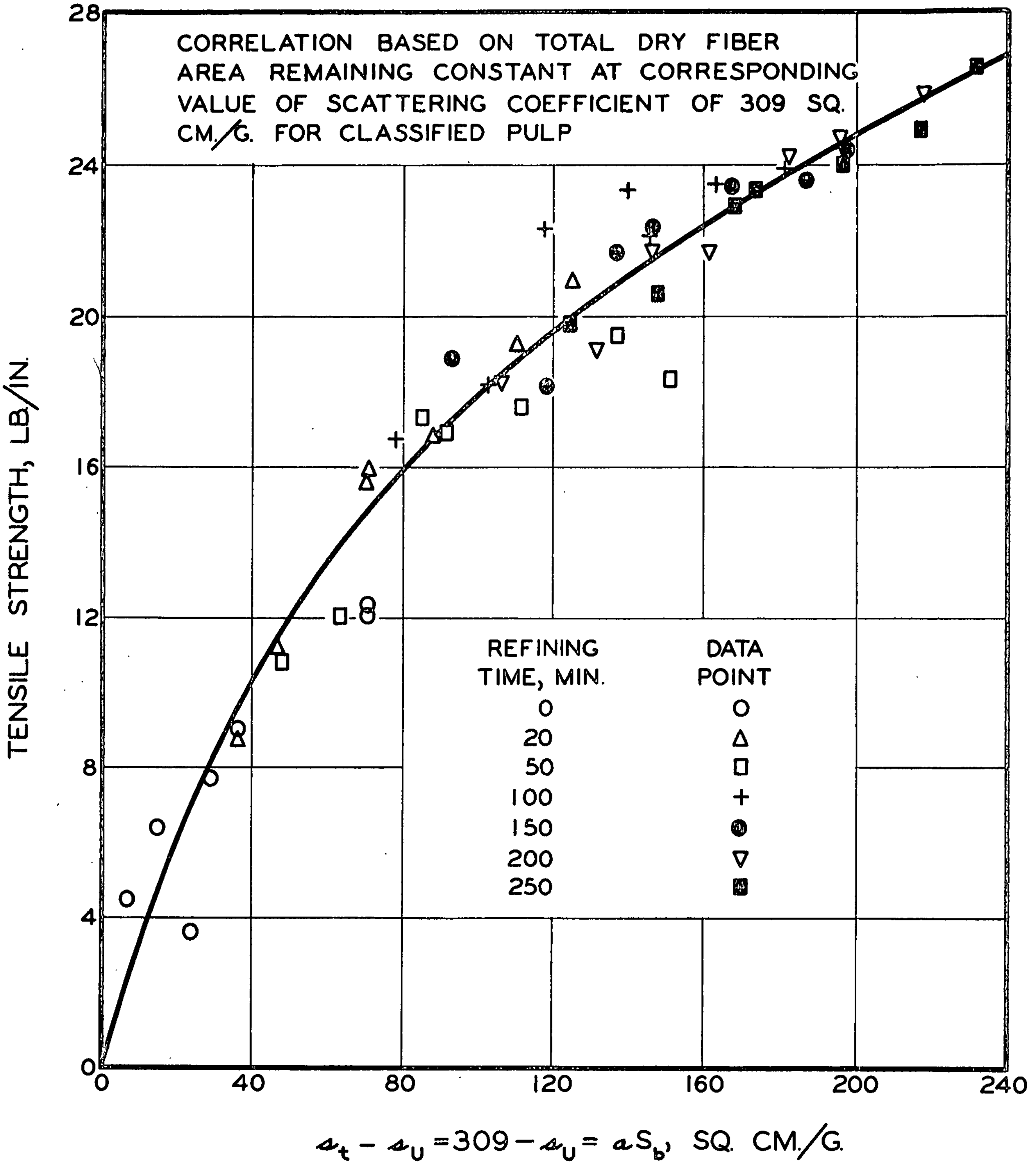

Figure 33

Tensile Strength-Total Bonded Area Relationship for Classified Pulp for Total Area Remaining Constant

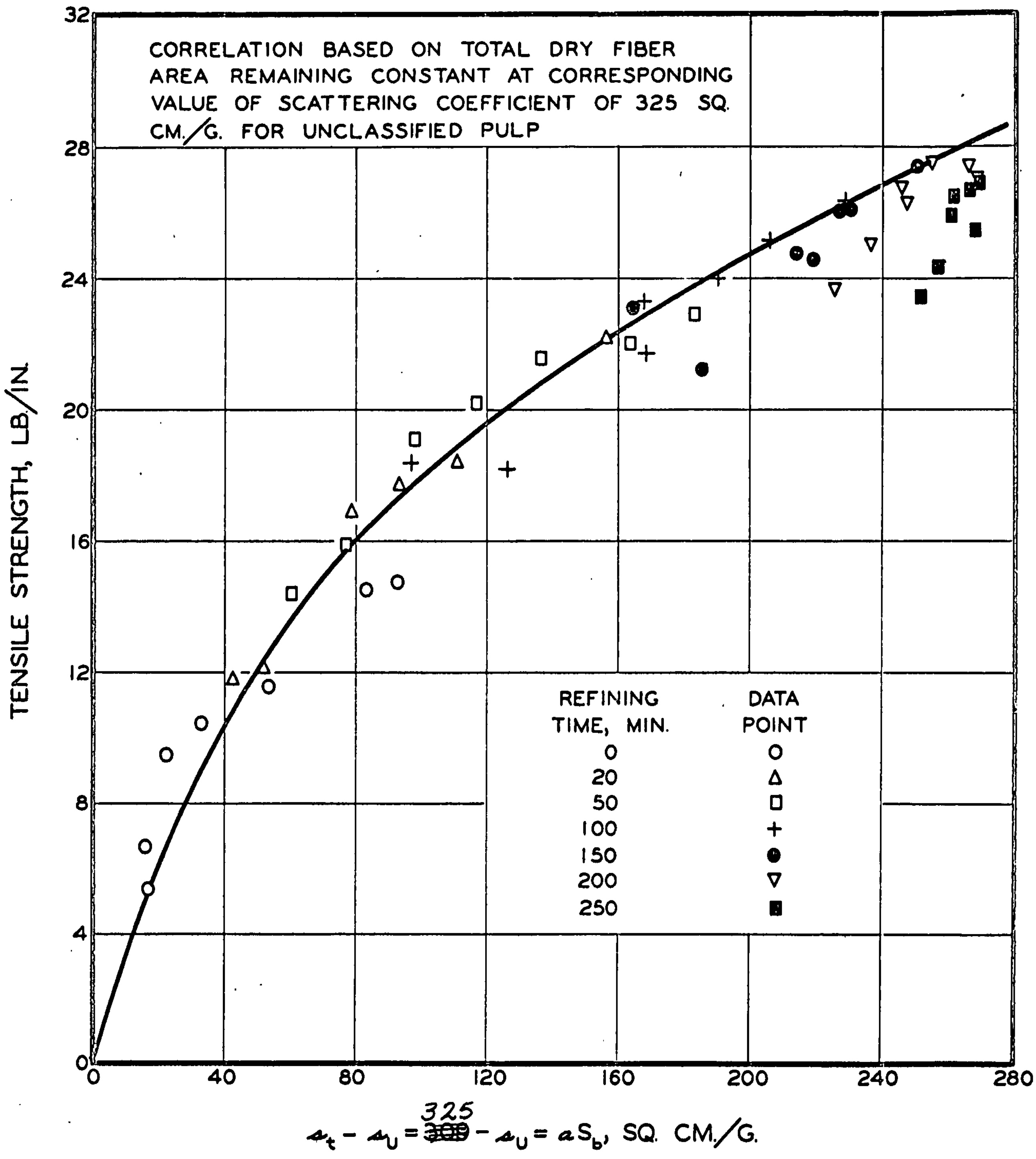

Figure 34

Tensile Strength-Total Bonded Area Relationship for Unclassified Pulp for Total Dry Fiber Area Remaining Constant remained constant. Of course, it would also be possible for an interaction of these variables to be such that the over-all contribution to strength remained constant. However, this is an unlikely possibility since the zero-span data, formation values, and microscopic measurements of fiber lengths did not indicate any appreciable changes with beating time. Also, Nordman and co-workers (42) have used a modification of the optical technique to estimate bonding strength and have reported no apparent change in bond strength with beating time for a number of pulps.

The shape of the curve relating tensile strength to total bonded area is dependent upon the relative amounts of fiber breakage and bond breakage in the tensile test. In Progress Report Six (43) it was shown that even with an unbeaten pulp (bleached sulfite), about 40% of the fibers in the zone of failure were broken, and beating to a freeness of about 320 cc. S.-R. increased the extent of fiber rupture to about 70%. Therefore, the curve of tensile strength as a function of bonded area will be one of continually decreasing slope, eventually going through a maximum and then showing a decrease in tensile strength as high degrees of mechanical degradation in the form of beating must eventually weaken the individual fiber strengths. The relationships in Figures 33 and 34 show that the rate of increase in tensile strength with respect to bonded area decreases as the amount of bonded area increases and fiber breakage becomes a more limiting factor. Maximum tensile strength was not reached in these studies, even with extensive ball milling of the pulps.

A different value for total bonded area may be calculated from Equation (3) by assuming the $\underline{s}$ values for butanol-dried fibers provide a measure of the increase in dry fiber area with refining when they are corrected by the ratio of the extrapolated $\underline{s}$ value to the $\underline{s}$ value measured directly for butanol values. This was the procedure recommended by Haselton (19), and the correction factor for the pulps, as previously calculated, is 0.75. This correlation between tensile strength and a number proportional to total bonded area, $\underline{aS}_b$, is shown in Figures 35 and 36. It is seen that a distinct family of curves is formed for the various beating intervals implying a considerable and probably unrealistic decrease in fiber strength, strength of bonds, or formation with increasing beating time. It is concluded that the use of $\underline{s}$ values for butanol-dried fibers indicates a spuriously large increase in fiber bonding that is ineffective in contributing to sheet strength, and hence this estimate of fiber bonding does not satisfactorily represent the mechanism of strength development in paper.

The relative or percentage bonded area as given by the ratio in Equation (2) of bonded area to total area available for bonding ($\underline{S}_b/\underline{S}_t$) may be estimated in a number of ways:

(1) The original Parsons (31) and Ratliff (32) technique assumes that $\underline{s}$ values for solvent-dried fibers are directly proportional to the total area available for bonding and uses the simple relationship of

$$\frac{S_b}{S_t} = \frac{s_t - s_u}{s_t} \qquad (2)$$

(2) Haselton's (19) concept of a correction factor for solvent-dried fibers to compensate for the difference in fiber shrinkage improves the accuracy of the calculation. Thus,

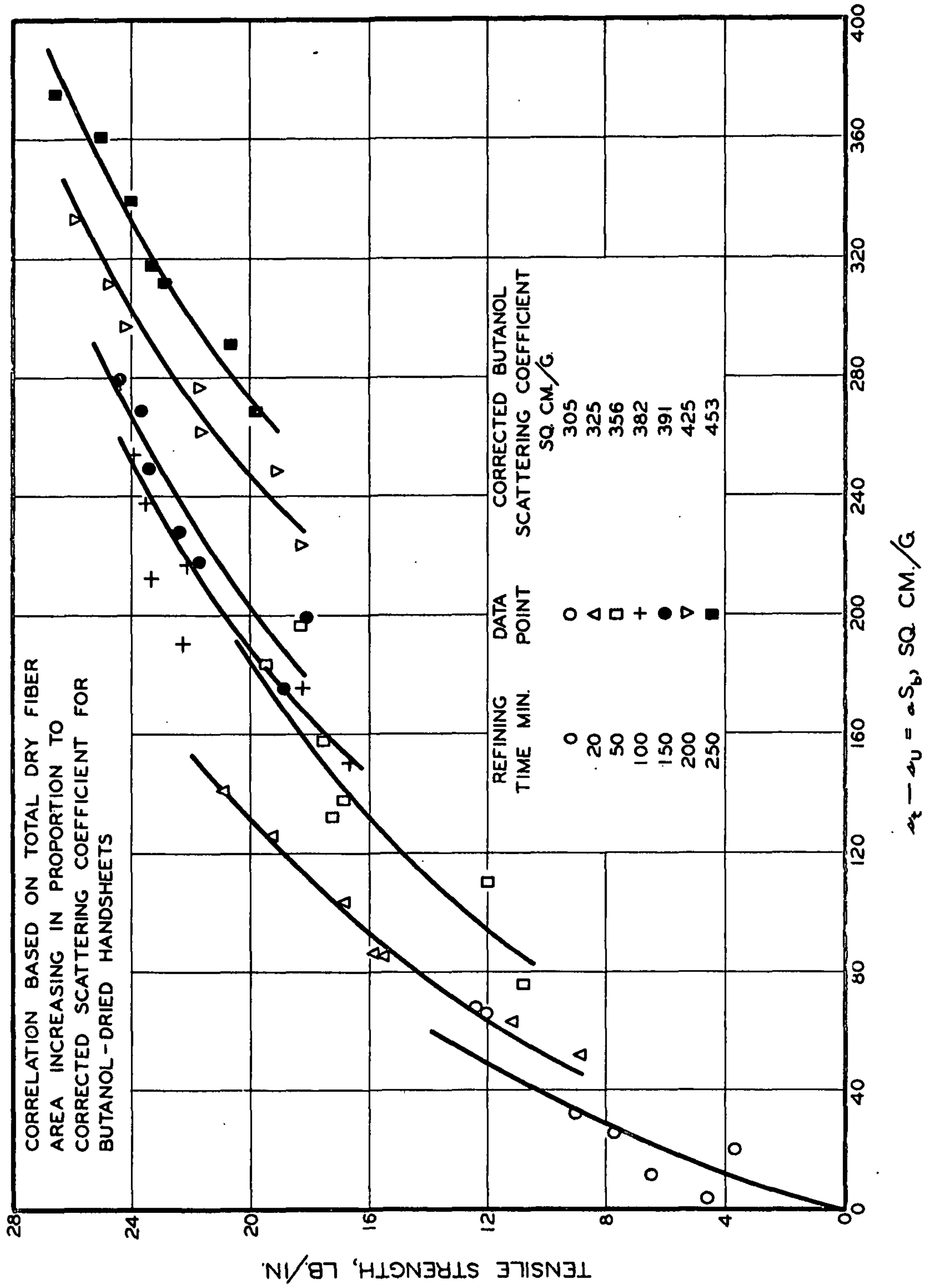

Figure 35
Tensile Strength-Total Bonded Area Relationship for Classified Pulp for Total Dry Fiber Area Increasing in Proportion to Corrected Butanol Scattering Coefficient

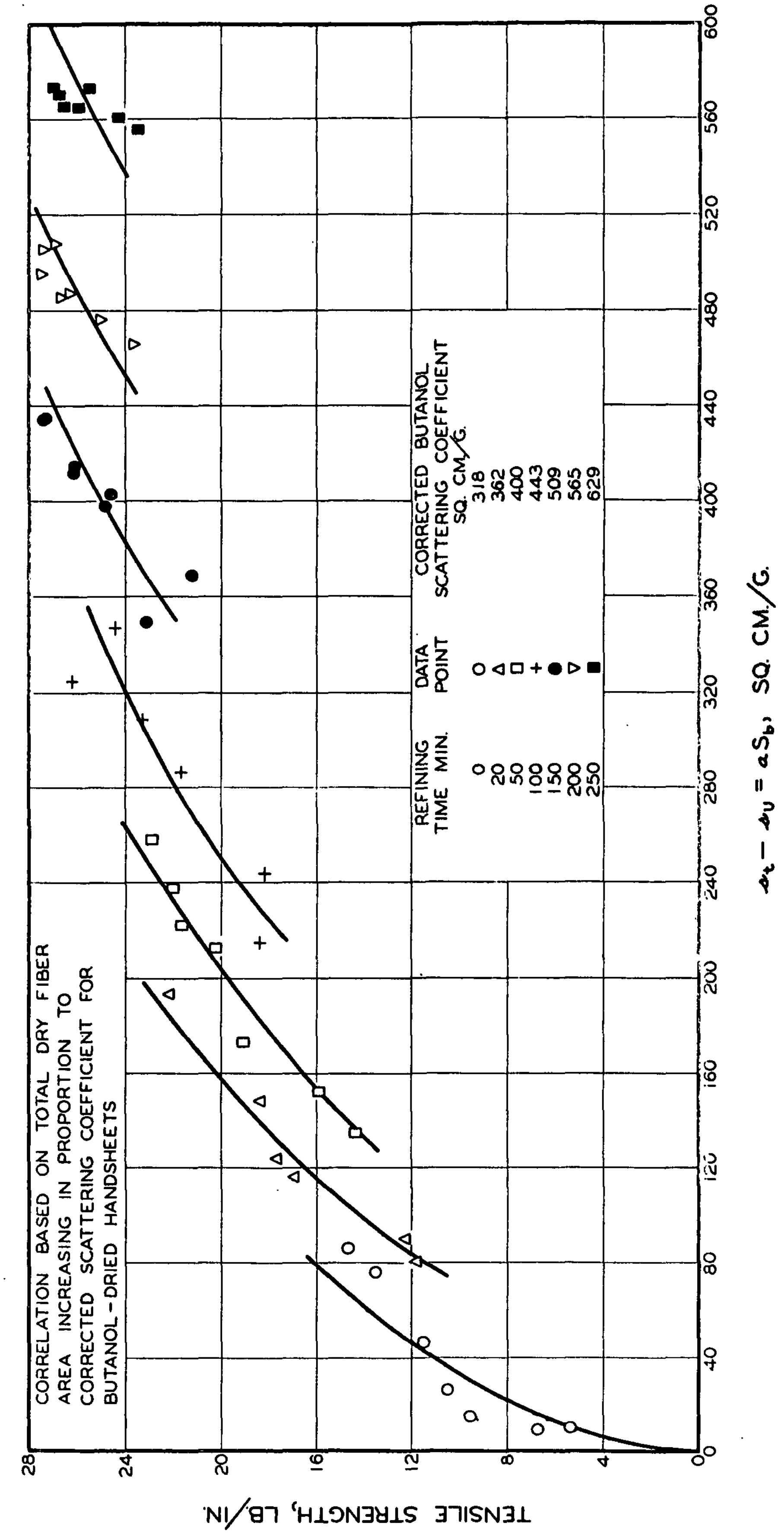

Figure 36

Tensile strength - Total Bonded Area Relationship for Unclassified Pulp for Total Dry Fiber Area Increasing in Proportion to Corrected Butanol Scattering Coefficient

$$\frac{S_b}{S_t} = \frac{s'_t - s_u}{s'_t} \qquad (2a)$$

where s'_t is obtained by multiplying the measured specific scattering coefficient for solvent-dried fibers, s_t, by the ratio of s for water-dried but unbonded fibers to s for unbeaten butanol-dried fibers.

(3) A slight improvement in Haselton's correction would allow for the fact that s has a small negative value for 100% bonded area ($S_u = 0$) because of the two handsheet surfaces. In this case $s = aS - 10$, and hence Equation (2a) becomes

$$\frac{S_b}{S_t} = \frac{s'_t - s_u}{s'_t + 10} \qquad (2b)$$

(4) Data from this study and previous work by Haselton have indicated that the total dry fiber area available for effective fiber bonding does not vary with refining, but may be characterized for a given unbeaten pulp by determining an extrapolated s value at zero tensile strength. This value of s remains constant and is designated by s'_{tc}. Relative bonded area is calculated by

$$\frac{S_b}{S_t} = \frac{s'_{tc} - s_u}{s'_{tc} + 10} \qquad (2c)$$

The four methods for estimating relative bonded area are shown in Figures 37 and 38 for classified and unclassified pulps. All four calculations show the same tendency for the rate of development of relative bonded area to decrease with increasing refining time. Each improvement of the estimate of relative bonded area generally lowers the level of the degree of bonding, and the most accurate of the estimates, based on the concept of constant dry fiber area, gives relative bonded

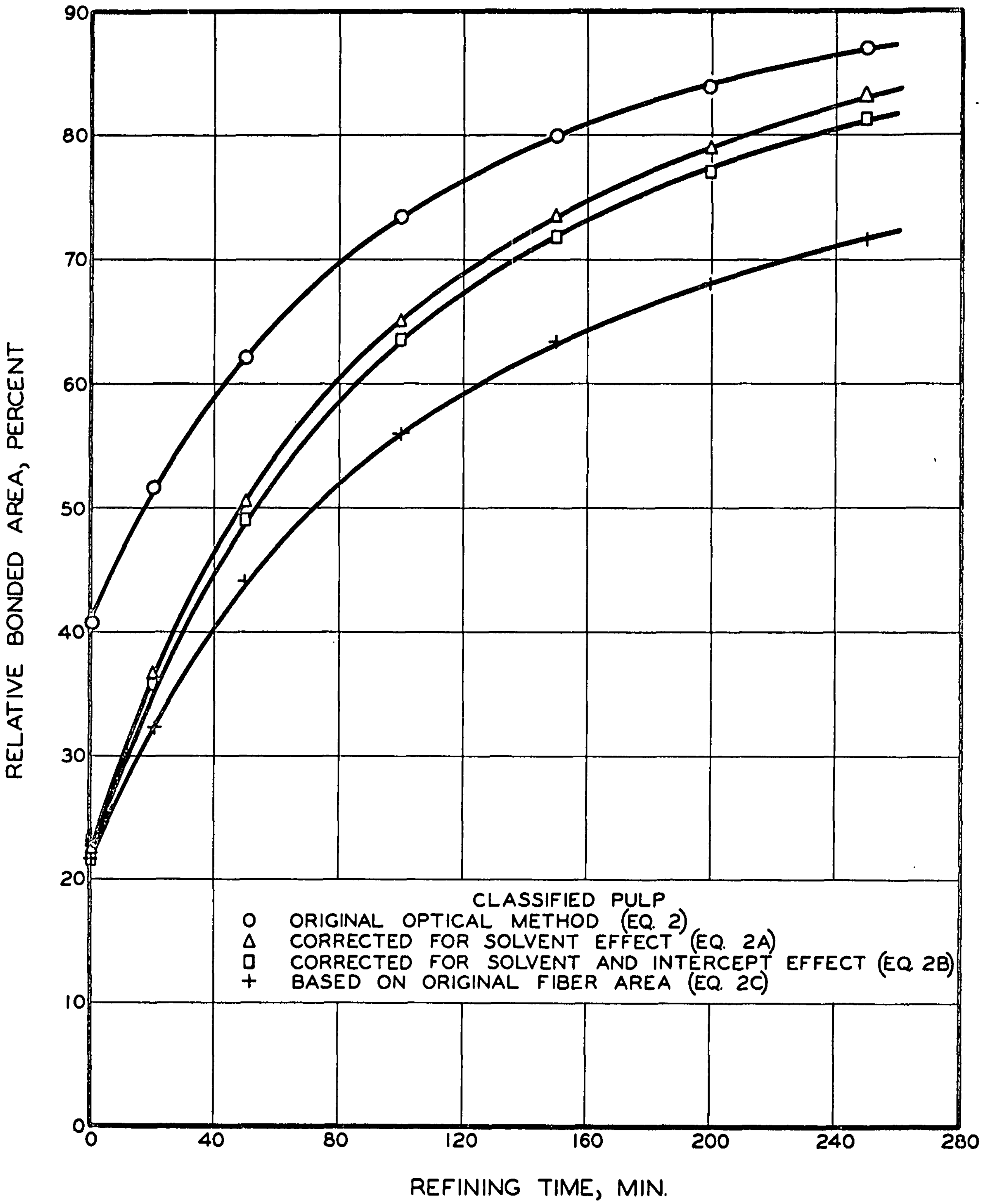

Figure 37

Relative Bonded Area for Classified Pulp as a Function of Refining Time

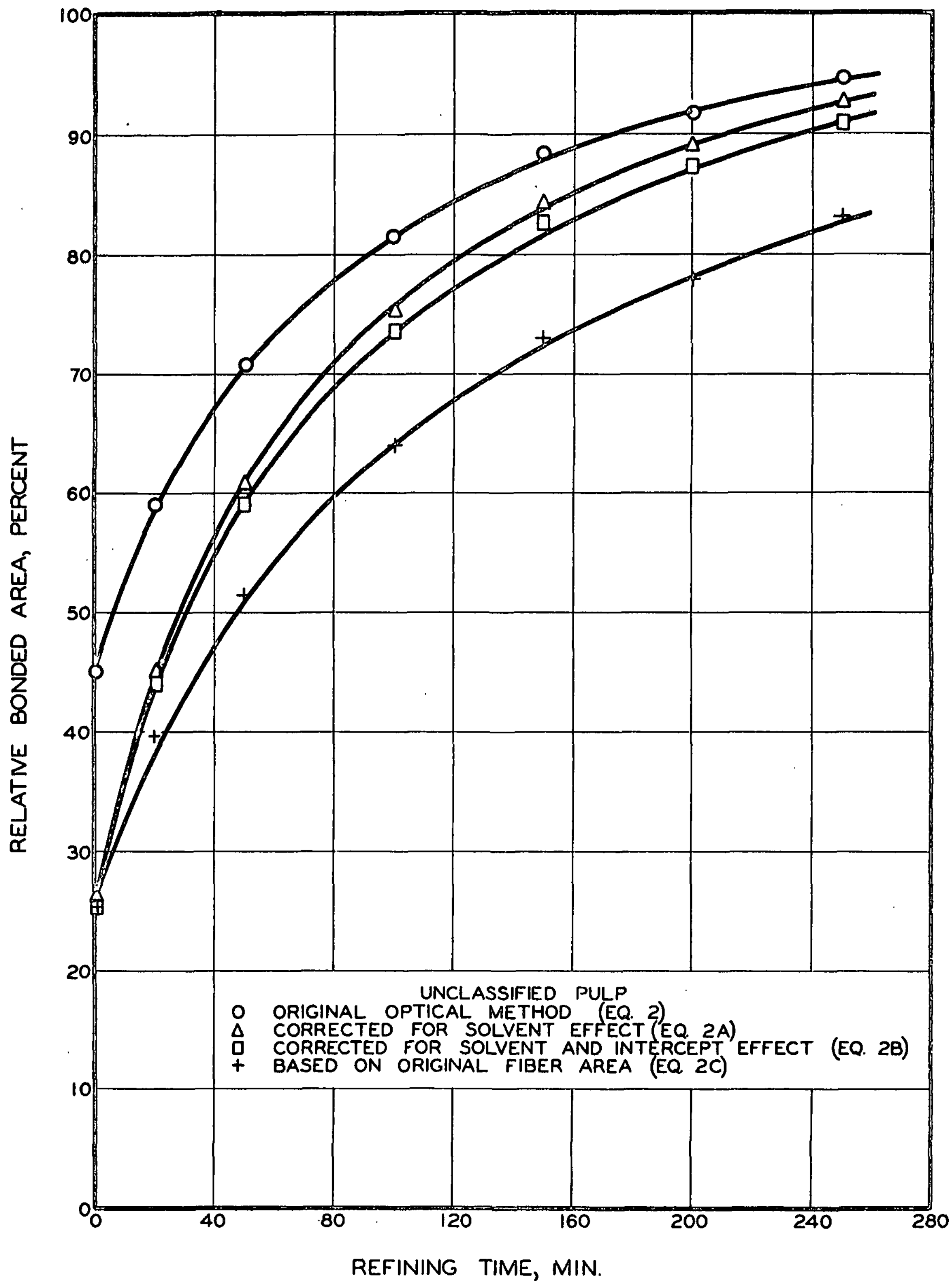

Figure 38

Relative Bonded Area for Unclassified Pulp
as a Function of Refining Time

areas about 20% lower than the original optical method, over the range of beating intervals shown.

The relative bonded area curve, based on the total dry fiber area remaining constant, can be regarded as having exactly the same shape as the total bonded area curve, since relative bonded area multiplied by a constant will equal the total bonded area. It has been demonstrated that at the same total bonded area, classified and unclassified pulps have the same tensile strength, and it is believed that this method of calculation gives a much more useful and reliable estimate of the extent of fiber bonding than do any of the techniques based on scattering coefficient values for butanol-dried fibers. Also, the level of relative bonded areas appears to be in a more realistic range than do the higher values obtained with butanol-dried fibers.

Previous analysis of the data has indicated that the bonded areas measured with the optical technique include intrafiber bonding of the lumen. Certainly intrafiber bonding and interfiber bonding would not be expected to contribute to sheet strength in a similar manner. It would be expected that tensile strength would be directly proportional to interfiber bonding of external fiber surfaces at relatively low values of bonded area whereas intrafiber bonding of lumen surfaces might be expected to affect individual fiber strength and therefore affect the tensile strength of paper at higher values of relative bonding where fiber breakage becomes an increasingly important factor.

As a first approximation, it may be assumed that the relative bonding of external fiber surfaces and internal lumen surfaces proceeds to the same extent upon increased wet-pressing or refining. If this is not the case, the relative bonded areas calculated by the optical technique would not provide a true picture of the extent of interfiber bonding of external surfaces since the lumen surface is appreciable compared to the external surface. For example, in this study it has been estimated that the dry fiber surfaces available for bonding consist of an external surface of 6850 and an internal lumen surface of 2550 sq. cm. per g. Consider a sheet in which 50% of the external surface has been bonded. If, at this degree of wet-pressing and refining, the available lumen surface is also 50% bonded, then the relative bonded area measured with the optical technique and Equation (2) is 0.50. However, if the extreme case is assumed to be that none of the available lumen surface was bonded at 50% bonding of external surface, the apparent relative bonding would be measured as only 36%. This extreme case is considered an unlikely possibility, and it is probable that the bonding of external surface and available lumen surface proceeds to roughly the same extent.

It is interesting to note that in Progress Report Seventeen (<u>44</u>), it was observed that apparently the individual fiber strengths of beaten fibers were about 25% greater than similar unbeaten fibers. It may be possible that a greater bonding of internal lumen surface in the case of the beaten fibers was responsible for the observed difference in individual fiber strengths.

Comment should be made on the observations of Nordman and Gustafsson (<u>45</u>) who correlated the specific scattering coefficient with tensile strength of pulps at various degrees of wet-pressing and refining in a Valley beater. These workers found, contrary to the results of this investigation (Figures 31 and 32), that when <u>s</u> was plotted against tensile strength, a series of linear relationships with about the same slope were obtained at each beating interval. It is possible in the case of refining in a Valley beater where a significant reduction in fiber length will occur, that the effect of fiber reduction will change the stress distribution in the tensile test or improve the formation or homogeneity of the paper specimen. In these studies, a ball mill-type action was chosen especially to minimize reduction in fiber length, and it was not a variable. Even in the case where fiber lengths were nearly constant, a correlation between s and tensile strength could form a series of curves over wide ranges of wet-pressing intervals at each beating interval, as indicated for a hypothetical situation in Figure 39.

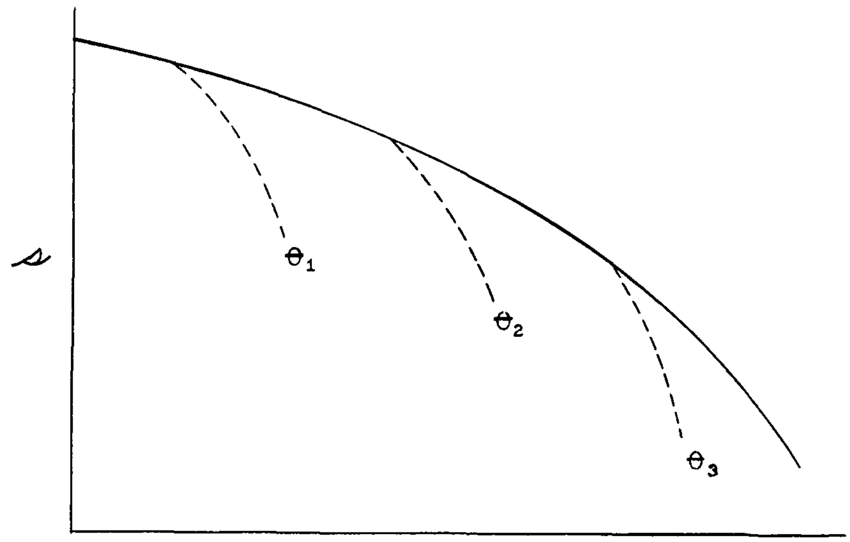

Figure 39

The solid curve represents various beating intervals, θ, at different degrees of wet-pressing over a relatively small range of wet-pressures. At some extreme in wet-pressure, it would be possible for the fibers to become permanently deformed so that the relative amount of internal bonding of lumen surface increases more than does the external bonding. In this case, the rate of increase in tensile strength with increase in total bonded area (external and internal) would become less, and a series of different curves, represented by dotted lines, would result. Therefore, the type of relationship shown by the dotted lines in Figure 39 would not necessarily imply an increasing available fiber surface with increased beating and extrapolation of the linear portions of the dotted lines to zero tensile strength, but would provide a false indication of an apparent increase in total fiber surface with beating time.

The specific scattering coefficient data which were obtained at wavelengths of 450 and 550 millimicrons were determined only for handsheets of standard wet-pressing intervals, and thus a comparison of relative bonded areas to values at 650 millimicrons may be made only with use of Equation (2) representing the original optical technique. The comparison between relative bonded area calculated from the specific scattering coefficients at the three different wavelengths is given in Table VI. It can be seen that there is a slight tendency for relative bonded area values to decrease with increasing wavelength, but the difference between the three sets of values is relatively small. Therefore, although the level of scattering coefficient depends upon the wavelength of light, the ratio of $\underline{s}$ values is about the same, indicating that the dependency of specific scattering coefficient on area ($\underline{s} = aS$) is significantly affected only by the value of the constant, $\underline{a}$.

TABLE VI

SCATTERING COEFFICIENTS OF BUTANOL AND STANDARD
HANDSHEETS AT DIFFERENT WAVELENGTHS

Unclassified Pulp

Refining Time, min.	Specific Scattering Coefficient, sq. cm./g.			Relative Bonded Area,* %		
	Wavelength, mμ			Wavelength, mμ		
	450	550	650	450	550	650
0, Butanol	495	456	429			
0, Standard	267	249	242	46.1	45.4	43.6
20, Butanol	561	519	488			
20, Standard	208	196	189	62.9	62.2	61.3
50, Butanol	608	571	539			
50, Standard	179	168	162	73.7	70.6	69.9
100, Butanol	715	640	596			
100, Standard	134	124	119	81.3	80.6	80.0
150, Butanol	829	731	685			
150, Standard	83	76	74	90.0	89.3	89.2
200, Butanol	896	817	761			
200, Standard	64	60	56	92.9	92.7	92.6
250, Butanol	1055	929	847			
250, Standard	65	60	56	93.8	93.5	93.4

Classified Pulp

Refining Time, min.	450	550	650	450	550	650
0, Butanol	456	424	400			
0, Standard	265	249	239	41.9	41.3	40.3
20, Butanol	477	447	426			
20, Standard	221	206	199	53.7	53.9	53.3
50, Butanol	540	489	466			
50, Standard	191	181	172	64.6	63.0	63.1
100, Butanol	593	529	501			
100, Standard	142	133	128	76.1	74.9	74.5
150, Butanol	610	548	513			
150, Standard	122	115	111	79.9	79.0	78.5
200, Butanol	663	590	556			
200, Standard	101	95	91	84.8	83.9	83.6
250, Butanol	707	623	594			
250, Standard	87	82	78	87.7	86.8	86.9

* Calculation based on regular optical technique, Equation (2).

E. CONCLUSIONS

The data have indicated that the total effective fiber area which is available for bonding remains constant and is unaffected by beating. Assuming a direct proportionality between specific scattering coefficient and fiber specific surface provides a convenient tool for estimating the relative bonded area in a sheet of paper from optical data. Knowledge of the amount of bonded area in paper is an important aid in the interpretation and correlation of strength properties, such as tensile strength, which are dependent on the amount of fiber-to-fiber bonding.

The problem of translating relative bonded area into absolute values of bonded area may be attacked by relating optical data to absolute areas as measured by gas adsorption techniques. Work of this type is currently in progress on the pulps used in the integrated studies. Comparisons of water-dried and solvent-dried fibers may be useful in determining the relative amounts of internal and external fiber area that are measured in the optical technique for estimating relative bonded area.

?

The author misses a very important point. The increased net area produced by pulping is lost by bonding upon drying in water, but the question is whether this is lost by self bonding or by bonding to other fibers. There is probably a simple ratio here & where the area available for bonding and the actual bonded area (between fibers) should both increase with refining. [illegible] 3/8/57

VII. FIBER SWELLING

A. SUMMARY

A comparison of wet fiber specific volumes measured by a modified Jayme centrifuge technique and a filtration method showed good agreement when precautions were taken to eliminate fines from the pulp used in the centrifuge test. The centrifuge values were about 7% higher than the filtration results because of the inherent inability to completely remove water from interfiber pores. Since the filtration method showed there is no difference in specific volume of classified and unclassified pulps, it should be possible to determine centrifuge values on pulps with fines removed and to check the method against filtration results to determine the extent of error introduced by retention of interfiber water. Once tested for a number of classified pulps, the centrifuge method would be a promising technique for measuring specific volume in a fast and efficient manner, suitable for routine control type work.

The data show that wet fiber specific volume is directly related to the ultimate amount of fiber-to-fiber bonding in paper. It is hypothesized that as beating proceeds and the specific volume of the fibers increases, the water-swollen fibers are in a more flexible state, and when wet pressed, the fiber surfaces are in more intimate contact and thus have more potential bonding areas. The rate of increase of bonded area for a given increase in specific volume becomes greater at higher levels of beating because the degree of fibrillation is also increasing and gives rise to larger surface tension forces drawing fiber surfaces together during drying. Because wet fiber specific

volume directly influences the degree of bonding in paper, it can, of course, be correlated with strength properties of paper. The nature of the correlation will be determined by the manner in which the property in question is affected by the extent of bonding. It is concluded that wet fiber specific volume as a measure of fiber swelling and fiber plasticity is an important pulp property and a useful pulp evaluation tool.

B. IMPORTANCE OF SWELLING IN STRENGTH DEVELOPMENT

The importance of fiber swelling in the ultimate development of strength in paper has been recognized and studied by many workers (28, 41, 46-49). In general it is believed that fiber swelling combines swelling of the cellulose gel in the fibers with opening of the fiber structure. It is uncertain whether or not the water which penetrates the intrafiber capillaries actually helps open these capillaries. It is certain that as fiber swelling increases, the fiber structure is in a more highly plasticized state. Thus, fiber flexibility becomes greater and greater conformability of the fibers is possible.

It is believed that this increased flexibility and plasticity leads to less fiber damage during the beating process and thus promotes more efficient wet beating. It is also reasoned that as fiber flexibility and plasticity are increased during beating, the more easily deformable fiber structure increases the interfiber contact during wet-pressing and hence leads to a greater number of potential bonding points on drying.

Gallay (50) has reviewed some of the methods that have been used to measure or indicate the degree of fiber swelling, among them being (1) direct microscopic measurement, (2) partial extraction, (3) dilatometric swelling, (4) centrifuge method, and (5) permeability technique. Of these methods, three were chosen (1, 4, 5) to characterize the pulps under investigation in the integrated study, and to attempt to make comparisons between the results of the three techniques.

C. EXPERIMENTAL

In the microscopic method of determining fiber swelling, fiber cross sections were prepared in a manner to correspond as nearly as possible to water-swollen fibers. The details of the preparation of the fibers is given in Appendix A-6. The cross sections were enlarged by a magnification of 1000X and were individually traced on paper. About 165 fibers from the unbeaten, classified pulp were analyzed and the cross sections are reproduced in Appendix B-3. No attempts were made to make cross sections of beaten or unclassified pulps because fines and fiber debris in these pulps cannot be properly evaluated or weighted in the microscopic determination.

The total fiber volume per unit mass of fibers was calculated by determining the product of cross-sectional area per fiber, average fiber length, and number of fibers per gram of pulp. The cross-sectional area per fiber was determined by weighing the total fiber cross sections cut from paper and multiplying by the area per unit mass of paper (corrected for the magnification factor).

The centrifuge technique was a modification of the procedure used by Jayme (47) and was described in some detail in Progress Report Fourteen (21). This method measures the so-called "water retention" value which is the mass of water associated with a unit mass of cellulose after centrifuging for a standard time. A centrifugal force of 1300 x gravity was used, and it was found that the interfiber water for the unclassified pulps could not be removed with this centrifugal force because of the high resistance to flow. Hence, data were obtained only for the classified pulps with the fines removed.

The permeability method, as originally developed by Robertson and Mason (7), determines a hydrodynamic specific volume which is equivalent to the specific volume measured in the constant-rate filtration technique reported in Progress Report Thirteen (9). Later modifications of the permeability method which was reported by Carroll and Mason (41) used classified pulp fractions to eliminate complications caused by the presence of high flow resistance fines. One of the advantages of the filtration method is that whole pulps with fines present may be evaluated. It was thus that data were obtained for the hydrodynamic specific volumes for both classified and unclassified pulps at all seven beating intervals used in the integrated studies.

C. WATER-SWOLLEN SPECIFIC VOLUME

The results of the microscopic, filtration, and centrifuge methods for determining water-swollen specific volume are summarized in Table VII. The original data for the latter two methods have been previously presented in Progress Reports Thirteen and Fourteen, respectively (9, 21), and the calculations based on the microscopic technique are shown in Appendix C-2.

TABLE VII

WATER-SWOLLEN SPECIFIC VOLUME

Beating Interval, min.	Microscopic Method, cc./g.	Centrifuge Method, cc./g.	Constant-Rate Filtration, cc./g.
0	~~3.08~~ 3.42	2.18	1.95
20	--	2.41	2.36
50	--	2.63	2.62
100	--	2.93	2.82
150	--	3.26	2.96
200	--	3.32	3.04
250	--	3.41	3.11

The previous filtration study showed that there was no difference between the specific volume of a whole and classified pulp at a given beating interval. This finding supports Carroll and Mason's results (41) which showed no significant difference in specific volume between different Bauer-McNett fractions of a pulp at given beating intervals. Hence, the values reported in Table VII for the filtration technique were determined from the averaged data for both classified and unclassified pulps (9).

The higher value of specific volume from the microscopic measurements compared to the other two methods was not readily explainable. However, work which is now in progress on the effect of certain dyes on rate of refining has indicated that Congo Red dye has a marked influence on increasing fiber swelling. Since the fibers under microscopic examination in this study were stained with Congo Red as an aid in viewing cross sections (Appendix A-6), it appears probable that the fibers were in an abnormally high state of swelling. Such slight differences in degree of swelling would have a strong effect on specific volume but a lesser effect on specific surface since in the former case the square of effective fiber diameter is involved, whereas in the latter case, specific surface is proportional to but the first power of diameter. Hence, the agreement previously noted in specific surface values is probably valid. However, because of the possible effect of dye on the swelling of the fibers, no comparison of the microscopic volume data with the other methods is justified.

The water retention values measured by a modified Jayme technique were converted to specific volume in Table VII by adding the pycnometric specific volume of cellulose in water to the mass of water per unit mass of cellulose as measured in the centrifuge method. A value of 0.62 cc. per g. was taken for the pycnometric density of bleached wood pulp (51, 52). For the average of the seven beating intervals, the water-swollen specific volume measured by the centrifuge technique is about 7% higher than the hydrodynamic specific volume determined in the filtration method. This is remarkable agreement, considering the differences in the two methods. Jayme (47) has recognized that one of the inherent difficulties in the centrifuge method lies in the inability to remove interfiber water completely. Thus, the water-retention value will always include some water retained in the pores of the wet mat. Therefore, it can be predicted that estimates of specific volume calculated from water-retention values will always be somewhat in excess of those determined in the filtration method for which water in the mat pores is not included in the hydrodynamic specific volume.

By working with a classified pulp, low flow resistance within the pad of pulp is encountered during centrifuging because of the absence of fines. It is this low flow resistance which brings about the good agreement between centrifuge and permeability estimates of swollen specific volume in the present work. Since it has been established experimentally that the swollen specific volume of classified and unclassified pulps is about the same, it should be possible to estimate the swollen specific volume of a given whole pulp by a quick centrifuge test on its classified sample. High hope is held for a routine control test based on these premises.

Since specific volume as measured in the filtration (or permeability) method is defined in a hydrodynamic sense, i.e., the volume of cellulose and associated water that is denied to fluid flow, it has been recognized that part of this specific volume may include water immobilized by fibrils. This does not appear to be the case from the experimental evidence, however. At higher degrees of refining, hydrodynamic specific volume appears to approach a constant value while external specific surface continues to increase linearly with time of beating. No "trapping" of any appreciable volume of water by these released fibrils is indicated by these data. It is important to note that the difference between specific volumes measured in the centrifuge and filtration methods did not show a significant trend to become larger at high degrees of refining, and it may be possible that the extent of fibrillation in a classified pulp does not appreciably affect the amount of interfiber water measured in the centrifuge method. At first thought, it would appear that the amount of interfiber water retained after centrifuging should increase with increasing fibrillation. However, it is possible that when air enters the wet mat being centrifuged, the flexible fibrils are bound tightly against the surface of parent fibers by forces of surface tension, with the result that the effective pore radius of the wet mat containing air does not decrease appreciably with increased fibrillation upon refining.

D. RELATIONSHIP BETWEEN SPECIFIC VOLUME AND DEGREE OF BONDING

The ratio of the volume of cellulose plus associated water to the total volume of a wet mat, i.e., the solid fraction, is given by the product of wet swollen specific volume, $\underline{v}$, and apparent mat density, $\underline{c}$. The water that is included in this so-called solid fraction, $\underline{vc}$, is not free to move under fluid driving forces and would represent the minimum moisture content of a wet mat if all the interfiber water could be removed from the pores of a mat.

To mechanically reduce the moisture content of the wet mat below this minimum value would require application of pressures large enough to deform the fiber structures and thereby displace water from pores of the cell wall and the lumen of the fiber. By using very high pressures for relatively long times, it was shown in Progress Reports Eight (53) and Ten (54) that all the interfiber water may eventually be removed. The exact pressure range in which fibers begin to deform is not known. However, drainage studies have indicated that the wet specific volume is not appreciably decreased up to several pounds per sq. in. compacting pressure. The estimated pressure on the wet fibers in the centrifuge test used in these studies was about 15 p.s.i. and Jayme has reported centrifuge data at about 25 p.s.i. with no indication that intrafiber water is being removed.

Hence, as a first approximation, it is probable that relatively little, if any, intrafiber water is removed with standard handsheet wet-pressing at 50 p.s.i. (the moisture content of standard wet-pressed handsheets is well above the minimum value which would be calculated from the wet specific volumes). Therefore, it would be expected that the solid fraction of a handsheet after wet-pressing would be approximated by the product of wet specific volume and apparent handsheet density (vc). If, as indicated by filtration compressibility data, apparent wet mat density, c, is about the same at a given pressure for all degrees of refining, then the handsheet solid fraction would be directly proportional to wet fiber specific volume, v.

The above indicated dependency of wet handsheet solid fraction upon the wet fiber specific volume is the basic reason for anticipating a good correlation between wet specific volume and the degree of bonding in the final dry paper. The greater the solid fraction of a wet handsheet, the more intimately the wet fiber surfaces must be in contact and therefore larger amounts of ultimate fiber-to-fiber bonding would be predicted for increased wet handsheet solid fraction. In Figure 40, the correlation between wet fiber specific volume, as measured by the filtration method, and the relative amount of fiber bonding (as calculated in the previous section of this report) is shown for classified and unclassified pulp. The correlation is excellent, and the data show that the rate of change of relative bonded area with respect to specific volume increases for higher degrees of beating. This concave upward characteristic of the curves would be anticipated, ~~and hence~~ since the Campbell effect (55), i.e., surface tension forces during drying, would be considerably greater. It is also possible that the release of "cementing

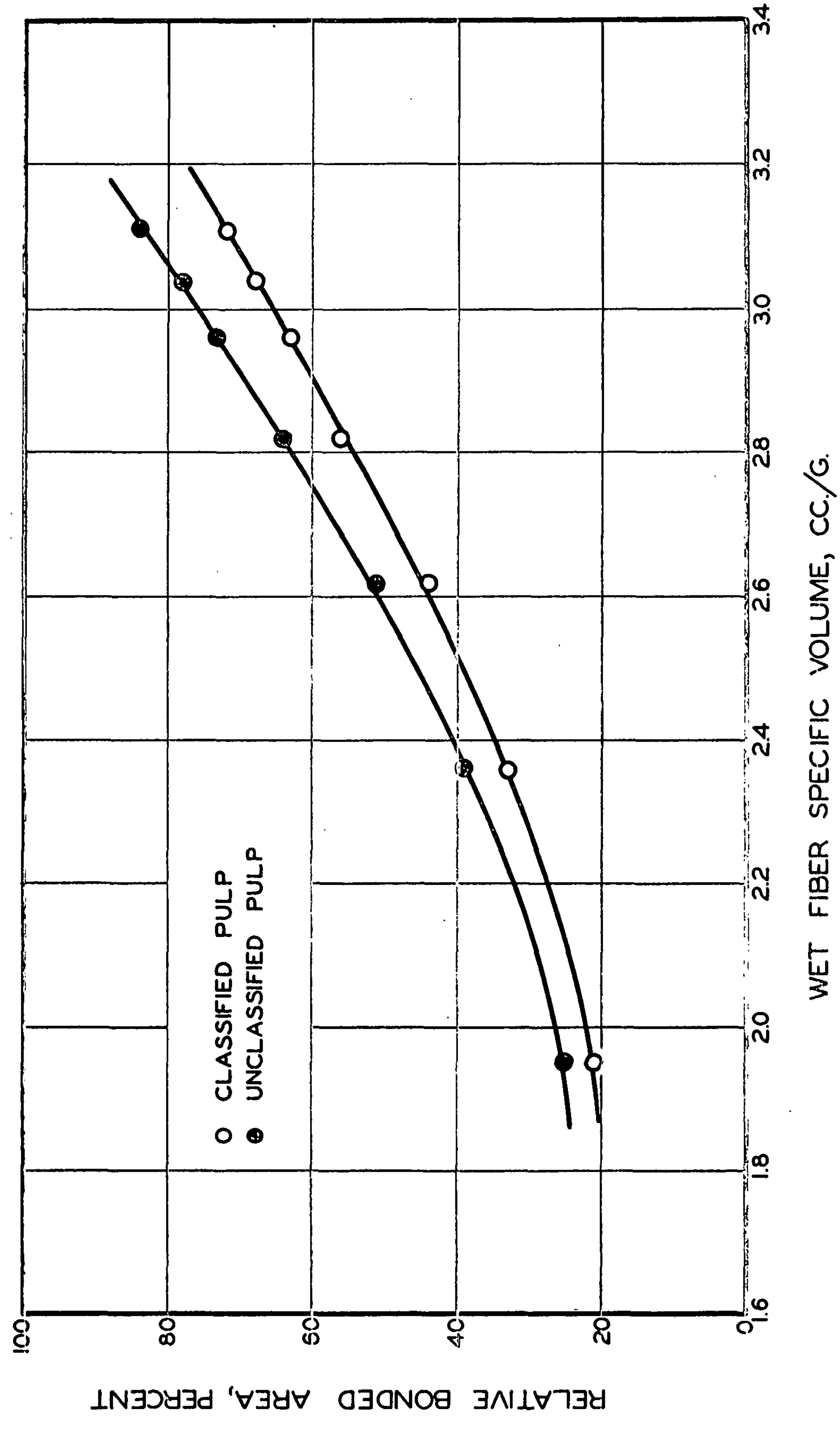

Figure 40

Relative Bonded Area as a Function of Wet Fiber Specific Volume substance" becomes greater at high beating times. Thus, the increase in bonding for a given increase in specific volume (the slope in Figure 40) would become greater as beating increases the extent of fibrillation and the extent of release of cementing substance.

The relative bonded areas shown in Figure 40 are equivalent to the total bonded area in the handsheet since they are based on the concept (established in the previous section of this report) of a constant total dry fiber area available for bonding. Because it has been shown that the unclassified pulp has a slightly higher dry fiber area available for bonding than does the classified pulp, at a given specific volume the relative bonded area of the unclassified pulp is greater than for the classified pulp. This is shown in Figure 40.

The relationship between wet fiber specific volume and strength properties of a handsheet is dependent upon the extent to which the strength property in question depends upon relative bonded area. It has been proposed that wet fiber specific volume fixes the wet handsheet solid fraction at a given degree of wet-pressing. Increased values of wet handsheet solid fraction give greater amounts of fiber-to-fiber bonding because of the more intimate contact of fiber surfaces. The nature of the quantitative relationship between relative bonded area and wet fiber specific volume depends upon the extent of fibrillation, and this factor will influence the nature of the correlation between specific volume and handsheet strength properties. An example of this type of correlation is shown in Figure 41 where tensile strength of the standard handsheets is related to specific volume. Two distinct curves are formed showing that at a given specific volume the unclassified pulp

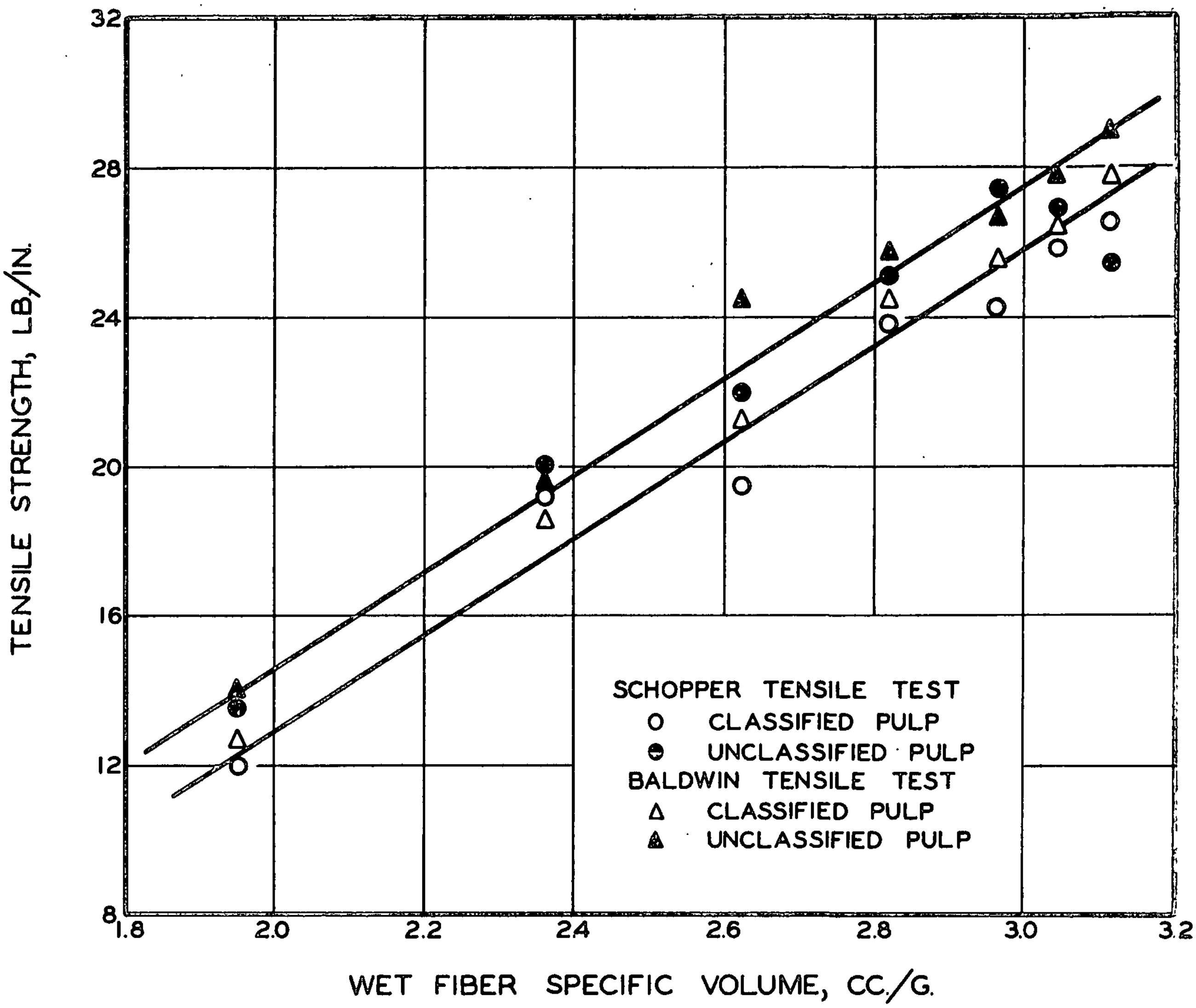

Figure 41

Tensile Strength as a Function of Wet Fiber Specific Volume has a tensile strength about 2 lb. per in. greater than the classified pulp. The linear relationship shown is probably fortuitous since the concave upward nature of the relative bonded area versus specific volume curve counterbalances the concave downward nature of tensile strength versus relative bonded area curve.

A more rational viewpoint of the effect of wet fiber specific volume on strength properties may be obtained by considering specific volume to influence relative bonded area as shown in Figure 40 and then to consider the relationship between strength characteristics and relative or total bonded area. For example, when the tensile strengths of the standard handsheets are correlated with the total bonded area, a common curve results for both classified and unclassified pulps. These data are shown in Figure 42 where the curve drawn through the data points was established from the more extensive tensile strength data shown in Figures 33 and 34.

Wet fiber specific volume is a useful property for predicting the amounts of fiber-to-fiber bonding, and hence, for estimating strength properties which depend upon the extent of bonding. It is assumed that specific volume is a measure of wet fiber flexibility and conformability. More direct information may be obtained if actual measures of wet fiber flexibility and conformability are obtained in the future.

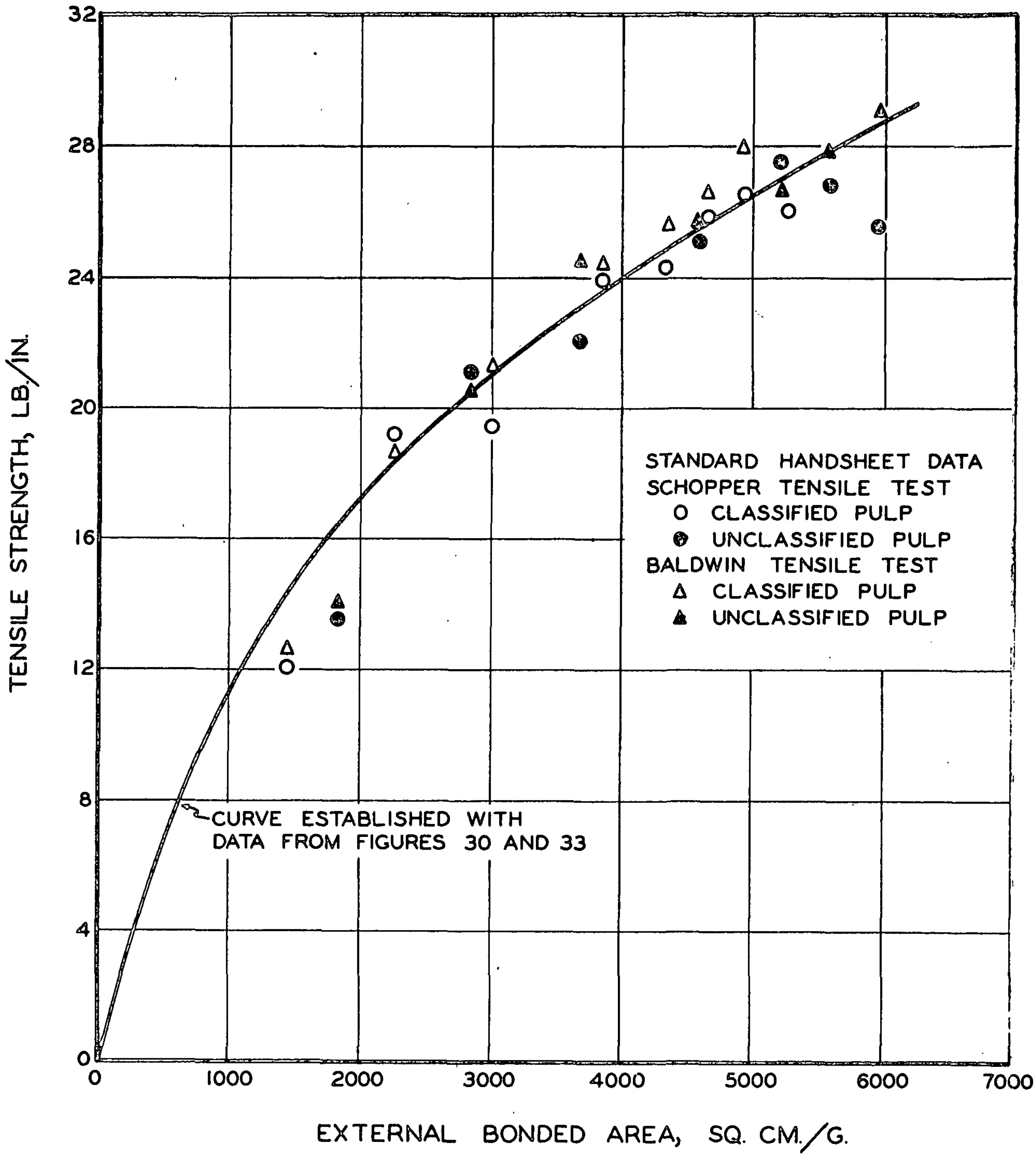

Figure 42

Tensile Strength as a Function of Total Bonded Area for Standard Handsheets

VIII. FACTORS CONTRIBUTING TO SHEET STRENGTH

A. GENERALIZED HYPOTHESIS OF SHEET STRENGTH

In correlating the known information on factors contributing to the strength of a sheet of paper, the point has been reached where an over-all hypothesis may be advanced. The construction of this hypothesis is given in the following paragraphs in terms of representative phenomenological properties proceeding from individual basic factors.

1. The Inherent Fiber Strength: First, among the representative properties, is the inherent tensile strength of the wood pulp fiber. This complex property depends on such basic factors as the moisture content of the fiber at the time of test, the fiber morphology and other genetic characteristics, the amount of degradation during pulping and bleaching, and probably changes in chemical composition during such processing. Possibly the extent of internal bonding also comes to play in this phenomenon. Results of individual fiber strength studies on Project 1513 have added to our knowledge of inherent fiber strength and its relation to sheet test results.

2. The Inherent Bonding Strength: Defined in terms of classified pulp, this property appears to depend on the chemical composition of the fiber surface and on the physical structure of same. Very little is presently understood about this property.

3. The External Specific Surface of the Unbeaten Fiber: Data presented in this report indicate that the external specific surface of the unbeaten fiber may be one of the determining factors in sheet strength. However, controlled experiments contrasting pulps from

various sources will be required to establish the relationship.

4. Fiber Conformability: This phenomenological property requires some explaining. The basic fiber property involved is that of fiber flexibility but this is modified by the maceration or "wet beating" of the pulp during processing and also by the wet-pressing of the formed sheet. Wet beating makes the fiber more conformable by making it more flexible; wet-pressing overcomes fiber stiffness and enforces conformability. These factors have been evaluated in the present study, but further work is needed on maceration of pulp in beating engines other than a ball mill.

5. Swollen Specific Volume: The property of water-swollen volume certainly depends on wet beating just as does the previously discussed property of conformability. Also, there is no doubt that increased swelling and plasticity favor conformability. Yet, at the moment, there may be reason to consider the properties of conformability and swollen volume as distinct. It is noted, for example, that the swollen volume approaches a constant value asymptotically as ball mill beating progresses but that the degree of wet beating, as measured by external surface development, continues to increase linearly with beating time. The development of tensile strength with time parallels the volume function, not the surface area function. Considerably more work with different grades of pulp is required in order to evaluate this matter.

6. Stress Distribution in the Sheet: For a given orientation, some average of fiber length and some sort of fiber length distribution function affect this property. The import of these factors is well

known from previous work, but their quantitative connection with strength properties has not been evaluated as part of a comprehensive view of sheet strength. So far in the integrated studies, fiber length effects have been deliberately minimized. This factor must be studied in future work.

7. Bonding Substance in Fines: Here is a property for which the only evidence is circumstantial and qualitative. Photomicrographs show that webs of something are present in unclassified pulp which are missing from classified pulp. The VVP and fold of classified pulp are much lower than those of the unclassified pulp. Also, the apparent density of the handsheets is different, although the swollen specific volume of the pulp is not. Qualitatively we have an idea of the role played by this property in sheet strength, but we have no idea what this "cementing substance" is. Also we do not know what part, if any, such substance plays in the phenomenon of fiber swelling on beating.

In view of the descriptions of properties given above, a status report may be made on the characterization of strength tests, as follows:

1. Tensile: Fiber conformability and swollen specific volume, properties 4 and 5 as enumerated above, have been analyzed for their effect on tensile strength in this report. Properties 3 and 6, the external specific surface of the unbeaten fibers and the stress distribution in the sheet have been analyzed in part in the published literature but must be thoroughly evaluated in the proposed integrated study of comparison of pulps. The role of the first two properties, inherent fiber strength and inherent bonding strength, has also been previously

evaluated and needs less work to be integrated into a quantitative analysis of paper tensile strength. The present work indicates that the seventh property - bonding substance - probably has but a minor effect on tensile strength.

2. Stretch: The last four properties enumerated above are of apparent importance to stretch. Broader interpretation will require quantitative evaluation of plasticity effects.

3. Burst: Since burst is a function of tensile and stretch, a basic interpretation of burst must await more information on stretch.

4. Fold: This is definitely a function of fiber conformability, inherent bonding strength, and bonding substance. It is thought that a better approach to understanding this strength test might be obtained by a study of fiber bonding strength.

5. Tear: When further data are obtained on inherent bonding strength, released bonding substance, and stress distribution, it will be possible to relate the physical analysis of the tear test to the properties listed above.

B. PULP STRENGTH PREDICTION

The logical question one may raise at this point is how may the various strength properties of a pulp be accurately predicted, given a hypothesis of sheet strength and correlations of the various tests such as those presented in this report.

It must be admitted that the parts of the puzzle not yet worked out preclude the offering of a scheme for pulp strength prediction at this time. Enough is known, however, to permit an educated guess as to what such a scheme would comprise when all needed information is at hand. A future phase of the integrated studies involving comparison of pulp of various types and processed in different beating engines is required to complete this scheme:

1. Basic Characteristics of Unbeaten Pulp

   a. External specific surface
   b. Swollen specific volume
   c. Inherent fiber strength
   d. Inherent bonding strength
   e. Inherent fiber stiffness
   f. Fiber length distribution

2. Beating Characteristics of Pulp

   a. Rate of development of swollen volume
   b. Rate of release of bonding substance
   c. Tensile *vs*. scattering coefficient
   d. Special physical tests

3. Beating Characteristics of Refiner

   a. Tendency to change fiber length distribution - whole fibers
   b. Relative tendency to release bonding substance or to produce discrete fiber fines
   c. Relative rate of development of swollen volume to external surface

At first sight, the battery of proposed tests appears indeed formidable - much more difficult than the present laboratory beater evaluation procedure. Outweighing this apparent disadvantage are two critical factors: First of all, the present laboratory beater and handsheet procedure is not satisfactory for prediction of what will happen in mill-scale refining equipment. Secondly, while the accumulation of the basic data required would be tedious at the outset, the indications are that the data required for day-to-day evaluations would be less complex than the present beater evaluations. For example, it should be possible, after one of the next phases of the integrated studies is completed, to characterize the beating engines in laboratory and mill as to their exact effects on pulp properties. With this information, a quick test of certain beating characteristics of the pulp, such as swollen volume, plus a few definitive tests on handsheets, such as scattering coefficient data, may enable a sound prediction of pulp behavior in papermaking.

C. PROGRAM OF FUTURE WORK ON THE INTEGRATED STUDIES

In the preceding discussion it was suggested that the factors in pulp evaluation might be conveniently broken down into three categories: basic fiber properties of a given pulp, processing characteristics of the pulp, and processing characteristics of the beating engine. So far, the integrated studies have touched on some items connected with the first two categories, but not at all with the third.

For future integrated studies, the first two categories listed above may be grouped together, and the last studied separately. The first two constitute a logical extension of the present study to other types of pulp, concentrating on the variables found to be significant in the present work and adding other evaluations now known to be called for. The comparative significance of fiber flexibility, of fiber length distribution, of swollen specific volume, of inherent bonding strength, and of released cementing substance could all be checked using ball-mill preparations of different types of pulps.

While all through the course of Project 1513 it has been argued that refining devices should be compared, no agreement has been reached on the most useful basis of comparison. As a result of the first part of the integrated sudies, we now know what tests and factors are of prime importance and we can make a more useful comparison of beating engines. Thus we can take, in a second portion of the continuing integrated studies, the general approach of treating one or two selected pulps in a variety of laboratory and mill beating and refining devices. The thought here would be to examine from a fundamental point of view how each of the devices produces strength improvement in paper. For example, exactly what the "cutting" of a Jordan or the "bruising" of a Hollander means in terms of stress distribution in the sheet, plasticization of the fibers, or surface available for bonding has never been evaluated. It is therefore proposed that the powerful new tools assembled for the first portion of the integrated studies be put to use on the problem of refiner action.

In the course of these two proposed extensions of the integrated studies, or in conjunction with them, the following unanswered or partly answered questions raised in the first portion of the studies should be explored:

1. The correlation studied by Haselton (19) between the surface area by gas adsorption of dried handsheets and the specific scattering coefficient of such sheets. [This work needs to be confirmed and extended to several different types of pulps.]

2. The effect of internal and external bonding of fibers on the inherent bonding strength as predicted by the technique of Nordman, Gustafsson, and Olafsson (42). [It is proposed to use nitrogen and krypton gas adsorption measurements in this investigation.]

3. The connection between velocity-viscosity product and bonding strength, in view of the discrepancies indicated between VVP data and bonding predicted from scattering coefficient data in the present work. [In a word, the present VVP data and the published data of Nordman et al. do not indicate the same effect - a reconciliation must be made.]

4. For individual fibers (not formed into a sheet) the relation between surface available to gas adsorption and specific scattering coefficient, and the connection of the same with the tensile strength of a single fiber. [It is obvious that gas adsorption determinations cannot be made on single fibers, but measurements made on an aggregate (unbonded) of single fibers can be correlated with the proper average of strength data on a number of single fibers.]

5. A series of cogent, related questions: Why must fines be produced on beating? What is the relative importance of the Campbell effect compared to development of specific volume? Can strength and specific volume be increased by some sort of beating process without any fibrillation also occurring?

6. The correlation of wet fiber flexibility with swollen specific volume.

7. The validity of approximating the swollen specific volume of pulps by use of the centrifuge technique for water retention. [In the present work a very good correlation between water retention values and swollen specific volume was observed. If experiments with other types of pulps bear out this as a general correlation, a great saving

in time for routine evaluations will be possible.]

In all this work, knowledge gained in the present investigation can be employed to make future work more precise and significant. For example, the knowledge of fines gained in the integrated study so far indicates the need to use classified pulp in any study where unknown fines loss can affect the results. The cumulative effect of observations such as these is to make the program increasingly effective as work goes on.

D. RECOMMENDATIONS

It is recommended that the Integrated Studies of Pulp Processing be continued for another three-year period with work proceeding along two major lines. One approach will involve continuation of the present ball-mill beating studies for various types of pulp; the other is to be concerned with a fundamental study of refining characteristics and their effect on sheet strength.

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X. APPENDIX

A. DETAILS OF PROCEDURES

1. BALL MILL REFINING OF PULP

For the purposes of this investigation, the reference pulp was wet beaten in a ball mill for various intervals. The demand of accuracy required that all pulp samples--including the unbeaten ones--be carefully disintegrated in the British disintegrator. To give all pulps a comparable treatment, the slushing procedures used for the zero interval pulp was given to all of the pulps beaten in the ball mill. In detail, this procedure is as follows:

> Three batches of 30 grams each of reference pulp were diluted to 2 liters with tap water at a temperature of $20\pm2^{\circ}$C. and disintegrated for 300 counts in the British disintegrator. All three of these charges were then dewatered and diluted to 2090 g. with tap water, also at $20\pm2^{\circ}$C. and disintegrated for an additional 3000 counts. Care was taken that the stirrer was mounted 2 inches from the bottom of the container.
>
> All ball mill charges were given identical treatments:
>
> The mill was prepared with 4546 g. of approximately 1-in. diameter porcelain balls. For the beating, a charge of pulp was poured into one of the ball mills and the residual contents of the container washed into the mill with 910 cc. of tap water. The revolution counter was set at 0, and the mill was operated for a given refining time. At the end of this time, the reading of the counter was recorded, and the batch of pulp was dumped. The pulp was beaten for intervals of 20, 50, 150, 200, and 250 minutes, and a total of 22 charges were prepared for each interval to obtain sufficient stock for all of the evaluation work that was to be carried out. To insure maximum accuracy and reproducibility, the balls were carefully weighed before and after the milling experiments and the same set of balls used in each mill.

The refined stock was dewatered on a Büchner funnel through a sheet of Cenco No. 13255 filter paper. All pulp for a particular refining interval was mixed thoroughly by being passed through the laboratory pulp breaker several times. Two quick moisture determinations were made to determine the approximate consistency of the pulp. Formaldehyde was added as a preservative, and the pulp was stored in double plastic bags at 5°C. until required for experimentation. Small portions of pulp from each refining interval were stored in a deep freeze (-10°C.) without formaldehyde for special testing in the future.

2. DETAILS OF BAUER-McNETT FIBER CLASSIFICATION

A portion of pulp from each beating interval was classified in the Bauer-McNett classifier to remove "fines." The classifier was set up with a graded series of screens, the last and finest being 150 mesh. Each classifier charge consisted of 30 grams of pulp which was diluted to 2 liters with tap water and disintegrated in a British disintegrator for 300 counts. Each charge was run through the classifier for 15 minutes, and the stock through 150 mesh was discarded. At the end of this time the contents of the four classifier tanks were combined in a muslin-covered wash box and the classifier thoroughly rinsed. The pulp in the wash box was allowed to drain without interference to prevent loss of fibers.

After every fifth classification run, the wash box pad was dewatered by hand and placed in a stainless steel pail. At the end of a day's operation, the muslin was thoroughly cleaned with a hose, and these washings were collected in a pail and dewatered. All such fiber collections were combined.

After every tenth run the screens were removed from the classifier and any adhering fibers washed into a stainless steel pail. The contents of this pail were dumped into a washbox and the classifier reassembled. Classified pulps were mixed in the laboratory pulp breaker. They were placed in plastic bags and a quick moisture content taken. The bags were then stored at 5°C. with 1% formaldehyde preservative.

3. DETAILED PREPARATION OF HANDSHEETS

Handsheets were prepared according to Institute Method 411. The same procedure was used for the preparation of classified and unclassified pulp handsheets, and is presented in some detail to indicate the care necessary for accurate, precise work.

Fifteen grams of ovendry pulp from a particular refining interval were diluted with 2 liters of tap water and disintegrated for 300 counts in the British disintegrator. Two charges were prepared in this manner. Both charges were poured into a 20-liter stainless steel kettle and diluted to 20 liters at a temperature of 20 ± 2°C. The pulp was then stirred by hand and 800 ml. of pulp slurry measured out to form a consistency sheet. The sheet was dried and weighed and the volume of slurry required to make a 1.2-gram handsheet calculated. Great care was taken that the hand stirring of the slurry was always done in a consistent, uniform manner. Also, the stirring of the stock in the sheet mold, couching and wet-pressing of the sheets was done as carefully as possible, using inspected press plates. Ten handsheets were formed from the slurry and the drainage time measured by TAPPI Method T 221m. These sheets were then pressed in a TAPPI sheet press according to Institute Method 411. Immediately after pressing, the according to Institute Method 411. Immediately after pressing, the sheets were placed on drying rings in the Humidity Room at 73°F. and 50% relative humidity. In all of the work, the same sheet press was employed, and only ten sheets were pressed at one time--a departure from conventional Institute procedures. A total of 50 handsheets were formed in this manner. From the remaining slurry, handsheets were formed but were not pressed. Wet handsheets were subsequently redispersed in water, stirred by hand, and dewatered on a filter paper in a Büchner funnel.

4. DETAILS OF CHEMICAL CHARACTERIZATION

Determination of Soluble Lignin

Bleached sulfite pulp yields a negligible Klason lignin residue, so acid-soluble lignin was determined spectrophotometrically on the Klason lignin residue filtrate to characterize both the unbeaten pulp and handsheets prepared at the various beating intervals. Klason lignin was determined by Institute Method 428. The absorption of the filtrate was measured at 230 mμ on a Beckman Model DU ultraviolet spectrophotometer. The concentration of the soluble lignin was calculated from the optical density of the filtrate using a value of 47.5 for the specific extinction coefficient.

Viscosity

The cupriethylenediamine disperse viscosity--a measure of the degree of polymerization of the pulp (D.P.)--was determined according to TAPPI Method T 230 using a capillary viscometer. Viscosity values were obtained at only one concentration, so that only an estimate of the D. P. can be made from this data.

5. DETERMINATION OF VELOCITY-VISCOSITY PRODUCT (VVP)

A measure of sheet tensile strength in a direction perpendicular to the plane of the paper was obtained with the IPC bonding strength tester as described in the references below. Briefly, the method consists of applying a film of oil whose behavior is Newtonian to a test strip of the paper. Dimensional analysis shows the product of the velocity of the wheel applying the film and the viscosity of the oil is proportional to the tensile stress in the nip between the paper specimen and the wheel. The endpoint of the test is that portion of the test specimen in which fibers are picked from the sheet surface, and the velocity of the wheel at this point is used to calculate VVP.

(a) Instrumentation Studies LXXIV, Tappi 35, no. 9:181-8A (Sept., 1952).

(b) Report 31 to: The American Paper and Pulp Association Instrumentation Program. Determination of the bonding strength of paper, Part V. Dec. 6, 1956.

6. MICROSCOPIC PROCEDURES

Common to all of the microscopic procedures, it is noted that standard Institute procedures were used in sampling the pulp slurries and diluting them to obtain the proper number of fibers on a slide, for the purposes of measurement for photography. All photomicrographs were taken on a fine-grain Panchromatic film with a green filter for maximum contrast.

Preparation of Photomicrographs

Preparation of Photomicrographs of Individual Fibers

These were prepared on two types of samples--the first were wet fibers which were merely mounted in water and photographed in the wet condition. In the second case, the photomicrographs of the dry fibers, a special drying technique was used. Fibers were removed from the water suspension and air dried on the tip of a needle. In this manner each fiber was dried individually so that the fibrils were not artificially restrained from movement during drying.

Beaten Fibers

Beaten fibers were air-dried on a slide for both classified and unclassified pulp photomicrographs.

Fiber Dimension Determinations

Fiber dimensions were determined on fibers that had been stained with Congo Red for better visibility. The pulps were sampled and diluted to get roughly 40 fibers on a slide. The slides were dried on a hotplate at 50°C. after the fibers had been lined up in roughly parallel orientation under a Greenough-type binocular microscope with the aid of dissecting needles. After drying, the fibers were covered with 2% glycerine in water and projected on a screen at 75 diameters. Length was measured to the nearest 0.1 mm.; fiber width was determined in roughly the middle of the fiber. At least 200 fibers were measured for each determination. Cross-sectional areas were obtained on the fibers by imbedding and cross-sectioning with a microtome, with the fibers in a condition corresponding as nearly as practical to the water-swollen state. The imbedding procedure has some effect on the swollen state of the fiber and hence its cross-sectional area, and is presented in detail.

> Fibers stained with Congo Red were immersed in 25% ethanol for 10 minutes, then transferred to 50% ethanol for 10 minutes, then 70% ethanol for 10 minutes, 95% ethanol for 10 minutes, and then to absolute ethanol for the same length of time. From the absolute ethanol the fibers were immersed in xylene for 10 minutes and then transferred to xylene saturated with Histowax for 1 hour. At the end of this time they were transferred to 100% Histowax of 53-55°C. melting point for 1 hour and then imbedded in this medium. These wax impregnated samples were cut to 10 micron-thick cross sections with a sliding microtome. The sections were fixed to a slide and flooded with xylene to remove the wax, and then the mounting completed with Canada balsam. Fiber images were projected on the ground glass of a photomicrographic camera at 1000 diameters and traced on tracing paper. The cross-sectional areas of these fibers were determined by cutting out the traced cross sections and weighing them. The total cross-sectional area of a particular field could be readily established by dividing the weight of the sample of these cross sections by the basis weight of the paper.

Determination of the Number of Fibers/Gram

The number of fibers per gram of pulp was determined by two procedures--the first, TAPPI Method T 232 sm-53, and the second Graff's Method, as reported in the Paper Trade J., 117, no. 17:25-31(Oct. 21, 1943). Both of these methods gave comparable results, and as they are fully described in the literature they are not described here.

B. SUMMARIZED EXPERIMENTAL DATA

1. Pulp Properties

2. Handsheet Properties

3. Fiber Dimensions

TABLE VIII

SUMMARIZED PULP PROPERTIES

	Refining Time, min.						
	0	20	50	100	150	200	250
Pulp yield, after removal of "fines," %	93.7	89.5	89.4	83.8	78.5	76.1	77.6
Schopper-Riegler freeness, cc.							
Classified	880	870	875	840	830	800	785
Unclassified	870	800	765	520	375	230	205
Handsheet drainage time, sec.							
Classified	5.0	5.3	7.6	5.4	7.2	8.5	11.1
Unclassified	7.2	6.0	6.3	12.6	44.2	85.1	172.7
Cupriethylenediamine disperse viscosity, cp.							
Classified	17.3	--	--	--	--	--	--
Unclassified	16.0	--	--	--	--	--	--
Alpha-cellulose, %							
Classified	85.5	--	--	--	--	--	--
Unclassified	84.3	--	--	--	--	--	--
Ash, %							
Classified	0.11	--	--	--	--	--	--
Unclassified	0.10	--	--	--	--	--	--
Soluble lignin, %							
Classified	0.42	--	--	--	--	--	--
Unclassified	0.53	--	--	--	--	--	--
Extractives, %							
Classified	0.19	--	--	--	--	--	--
Unclassified	0.33	--	--	--	--	--	--
Hydrodynamic specific surface, sq. cm./g.							
Classified	7700	9150	10,450	14,100	18,200	21,300	25,200
Unclassified	10,600	17,400	22,700	37,400	52,000	63,300	79,400
Silvering area, sq. cm./g.							
Classified	7650	9990	9600	11,180	10,680	11,960	10,700
Unclassified	8270	8820	11,200	20,820	16,620	18,700	20,100
Dye adsorption, mg./g., classified	1.42	2.00	2.28	3.01	3.57	3.65	4.26
Area, sq. cm./g., "	7450	10,050	11,950	15,800	18,750	19,150	22,350
Dye adsorption, mg./g., unclassified	1.62	1.85	2.38	3.12	3.70	3.86	4.03
Area, sq. cm./g. "	8500	9700	12,500	16,400	19,400	20,250	21,100
Jayme water retention value, %							
Classified	166.1	179.1	201.3	231.3	264.1	270.5	278.9
Unclassified	156.3	--	--	--	--	--	--
Wet fiber specific volume, cu. cm./g.							
Classified	1.83	2.25	2.58	2.89	2.95	3.00	3.11
Unclassified	2.06	2.38	2.67	2.80	2.93	3.05	3.00

TABLE IX

HANDSHEET EVALUATION - STRENGTH TESTS

	Refining Times, minutes						
	0	20	50	100	150	200	250
Basis weight, lb./25 x 40 x 500							
Classified	47.7	46.1	47.5	45.8	46.8	45.9	45.4
Unclassified	47.4	46.2	46.7	47.4	46.5	47.2	46.2
Caliper, mils							
Classified	4.0	3.4	3.3	2.9	2.8	2.8	2.7
Unclassified	3.7	3.2	3.1	2.8	2.7	2.6	2.6
Apparent density, basis weight/caliper							
Classified	12.0	13.6	14.4	15.8	16.7	16.4	16.8
Unclassified	12.8	14.4	15.1	16.9	17.2	18.2	17.8
Burst, pts./100 lb.							
Classified	47.9	78.5	88.2	100	103	109	114
Unclassified	58.9	88.1	101	106	109	102	107
Tear Factor							
Classified	2.28	1.50	1.35	1.07	1.03	1.02	0.95
Unclassified	2.05	1.23	1.05	0.91	0.84	0.74	0.74
Basis weight, lb./25 x 40 x 500							
Classified	47.7	46.9	47.9	46.5	46.3	45.7	46.9
Unclassified	47.4	46.4	46.9	47.8	46.6	46.4	46.8
Caliper, mils							
Classified	4.0	3.4	3.3	3.0	2.8	2.8	2.8
Unclassified	3.7	3.2	3.1	2.9	2.8	2.6	2.6
Formation, units							
Classified	50.6	50.8	35.9	38.3	28.9	30.5	34.8
Unclassified	49.2	49.7	36.6	30.5	31.5	39.7	49.8
Zero span tensile, lb./in.							
Classified	40.5	43.7	43.2	45.2	46.4	44.1	46.9
Unclassified	39.6	42.6	44.3	44.6	42.6	43.8	45.6
Baldwin tensile, lb./in.							
Classified	12.6	18.7	21.4	24.5	25.7	26.7	28.1
Unclassified	14.0	20.7	24.6	25.9	26.7	27.8	29.2
Baldwin stretch, %							
Classified	3.1	4.6	4.7	5.4	4.9	5.4	5.1
Unclassified	3.6	5.0	5.0	4.8	4.7	4.3	4.2
VVP (kp., cm./sec.)							
Classified	2.01	2.40	3.43	5.45	8.31	12.0	11.6
Unclassified	2.24	3.06	4.94	9.13	14.0	15.6	17.8

TABLE X

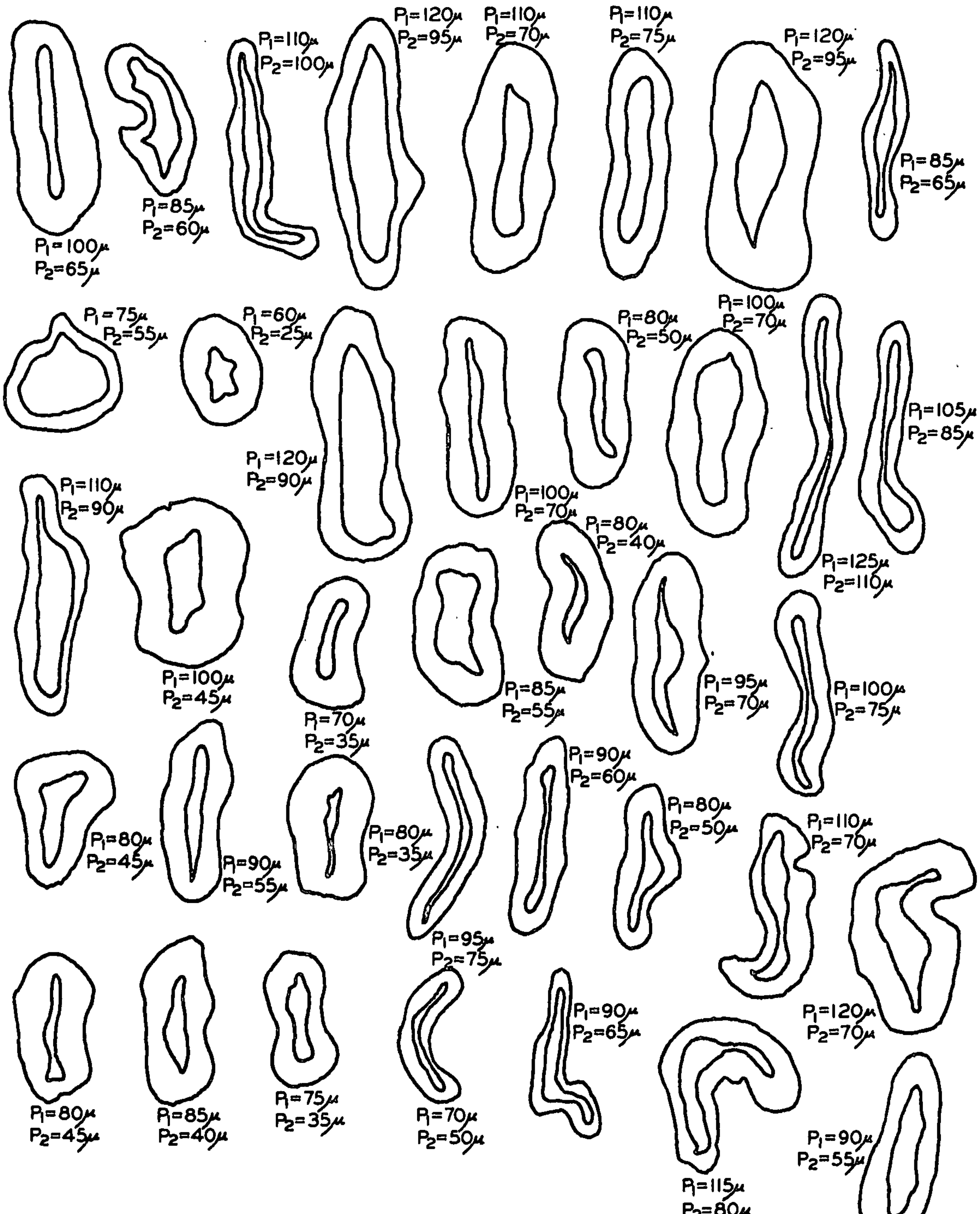
HANDSHEET EVALUATION - PHYSICAL PROPERTIES

Refining time, min.		0	20	50	100	150	200	250
Gurley porosity, sec.	Classified	1.0	29.0	110.0	1674	30,150	225,000	400 (hr./100 cc.)
	Unclassified	3.0	4.0	9	47.0	237	449	2893
Clark stiffness	Classified	64.4	57.3	55.7	45.6	41.8	33.0	38.3
	Unclassified	53.1	50.7	49.3	41.9	32.7	35.2	31.1
Clark rigidity	Classified	43.2	37.8	37.5	29.8	27.3	21.0	25.3
	Unclassified	35.4	33.1	32.5	28.2	21.4	23.0	20.5
Clark rigidity factor	Classified	67	96	104	110	124	96	115
	Unclassified	70	101	109	115	98	49	117
		Handsheet Pulp						
Silvering area, sq. cm./g.	Classified	7290	9750	6810	7580	9500	8110	10,100
	Unclassified	7160	9340	9900	11,000	12,000	16,160	20,500
Hydrodynamic specific surface, sq. cm./g.	Classified	7550	9400	10,700	14,800	17,700	21,100	26,750
	Unclassified	10,100	13,350	17,300	28,850	39,100	54,250	76,400
Wet fiber specific volume, cu. cm./g.	Classified	1.98	2.17	2.45	2.68	3.03	3.05	3.08
	Unclassified	1.92	2.38	2.58	2.81	2.93	3.05	3.00

TABLE XI

HANDSHEET PULP EVALUATION - CHEMICAL PROPERTIES

Refining time, min.		0	20	50	100	150	200	250
Cupriethylenediamine viscosity, cp.	Classified	17.1	17.2	17.8	18.0	17.7	17.3	16.3
	Unclassified	16.7	16.7	16.8	15.5	15.1	14.8	15.4
Alpha-cellulose, %	Classified	85.5	--	--	84.3	--	--	87.9
	Unclassified	84.7	--	--	86.2	--	--	90.7
Extractives, %	Classified	0.19	--	--	0.24	--	--	0.22
	Unclassified	0.38	--	--	0.49	--	--	0.33
Ash, %	Classified	0.15	--	--	0.50	--	--	0.21
	Unclassified	0.07	--	--	0.50	--	--	0.59
Soluble lignin, %	Classified	0.16	--	--	0.52	--	--	0.54
	Unclassified	0.28	--	--	0.22	--	--	0.22



P_1=PERIMETER OF FIBER, MICRONS
P_2=PERIMETER OF LUMEN, MICRONS

Figure 43

Wet Fiber Cross Sections (750X)

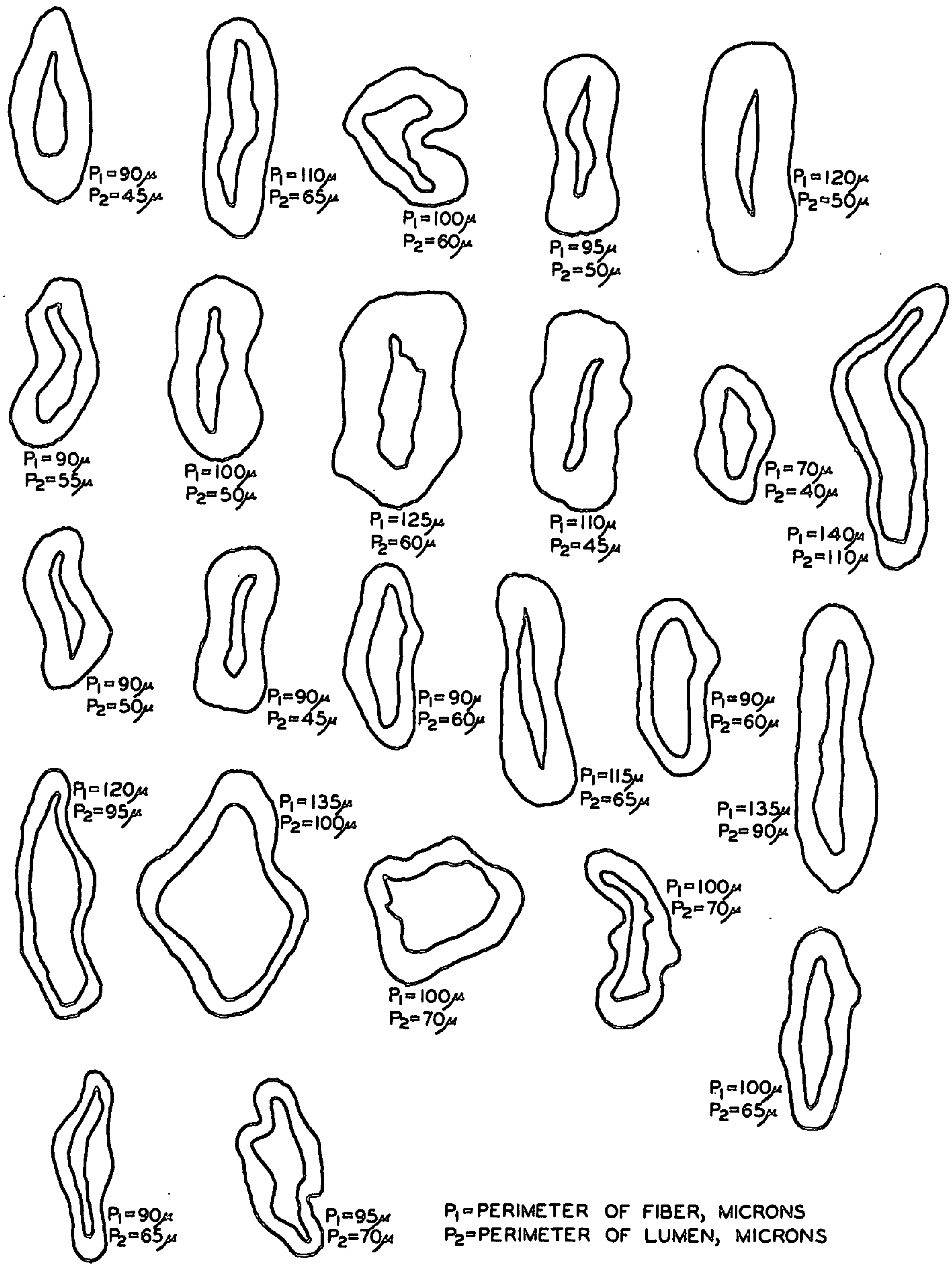
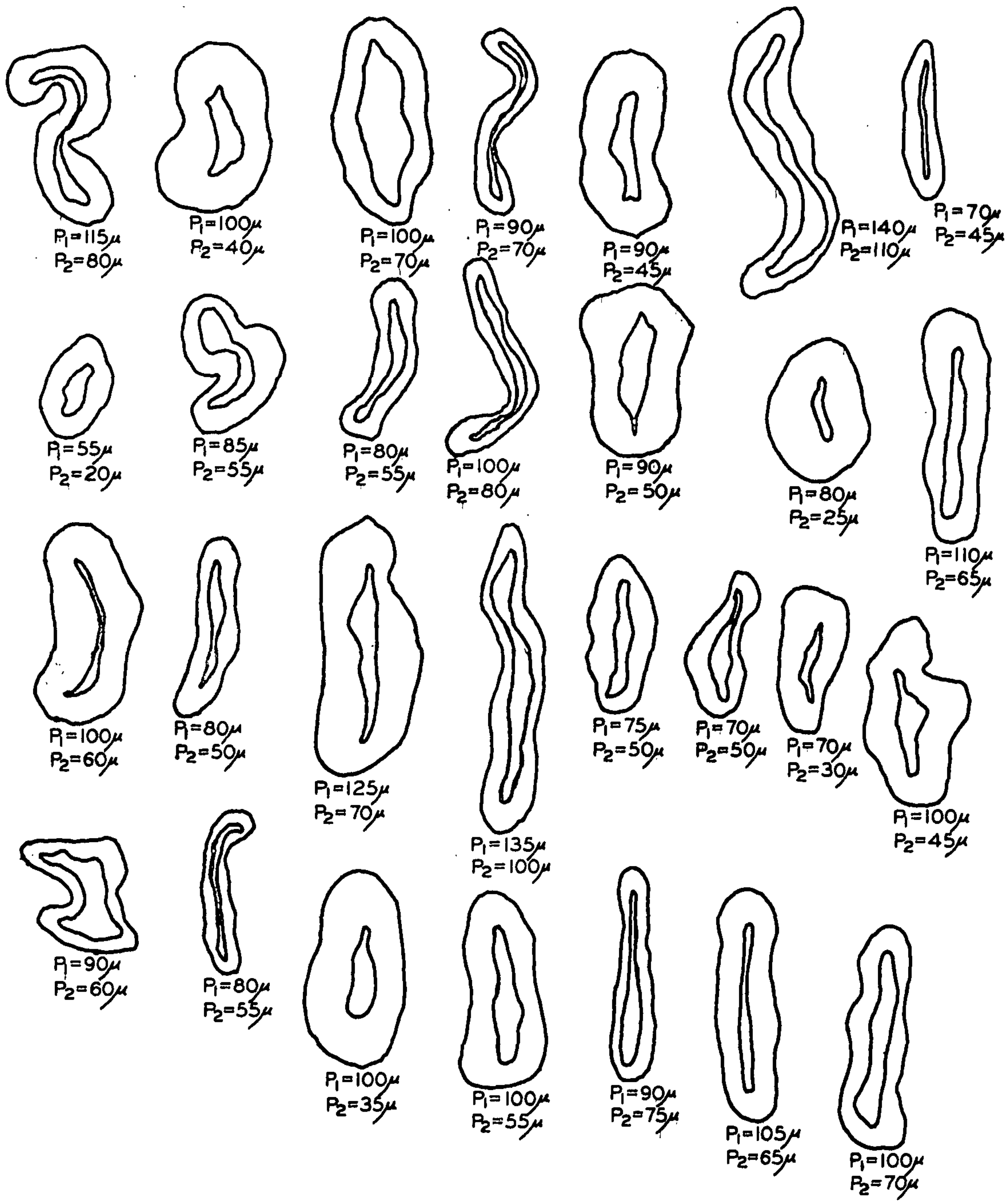


Figure 43 (continued)

Wet Fiber Cross Sections (750X)



P_1 = PERIMETER OF FIBER, MICRONS
P_2 = PERIMETER OF LUMEN, MICRONS

Figure 43 (continued)
Wet Fiber Cross Sections (750X)

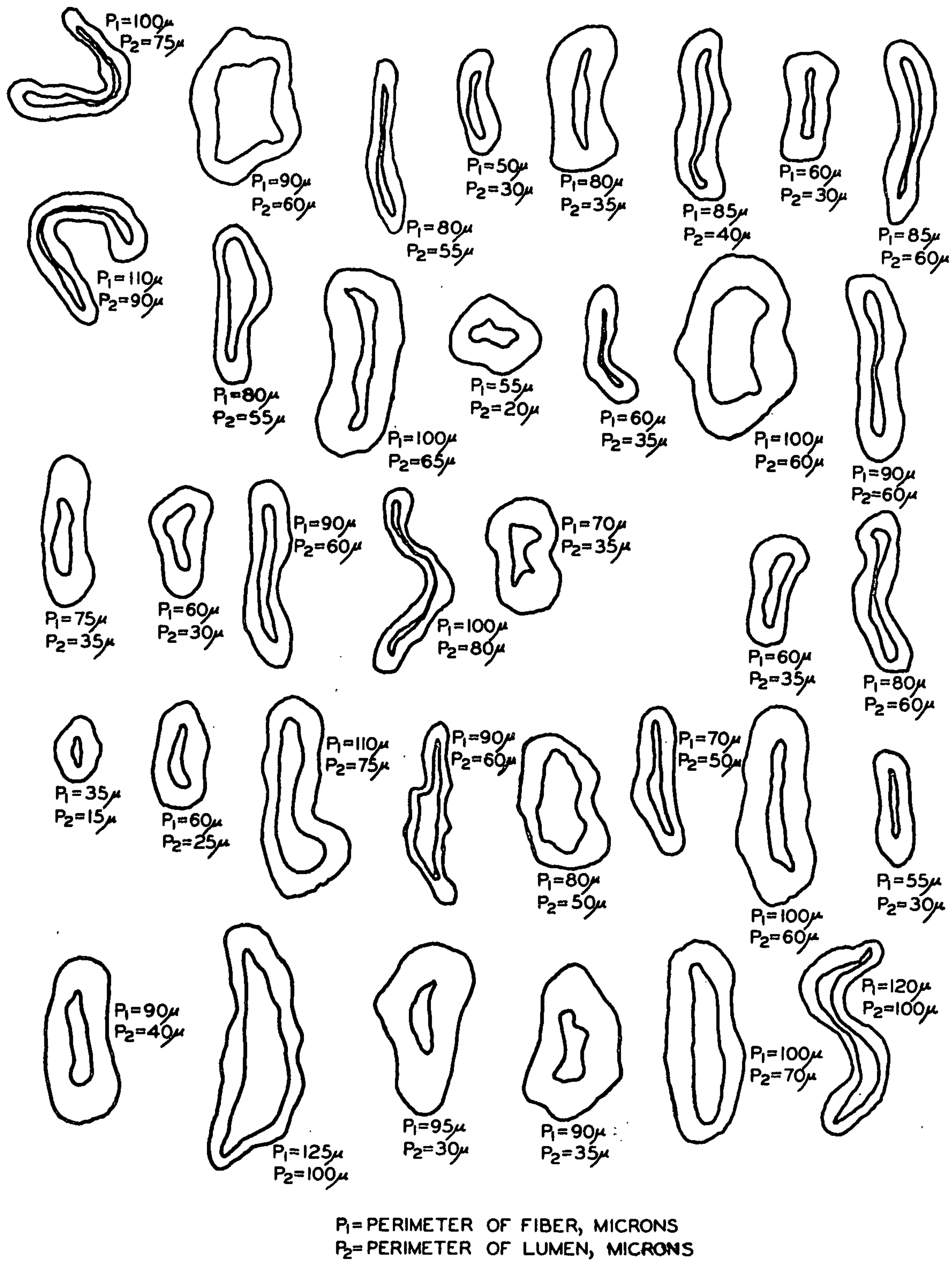
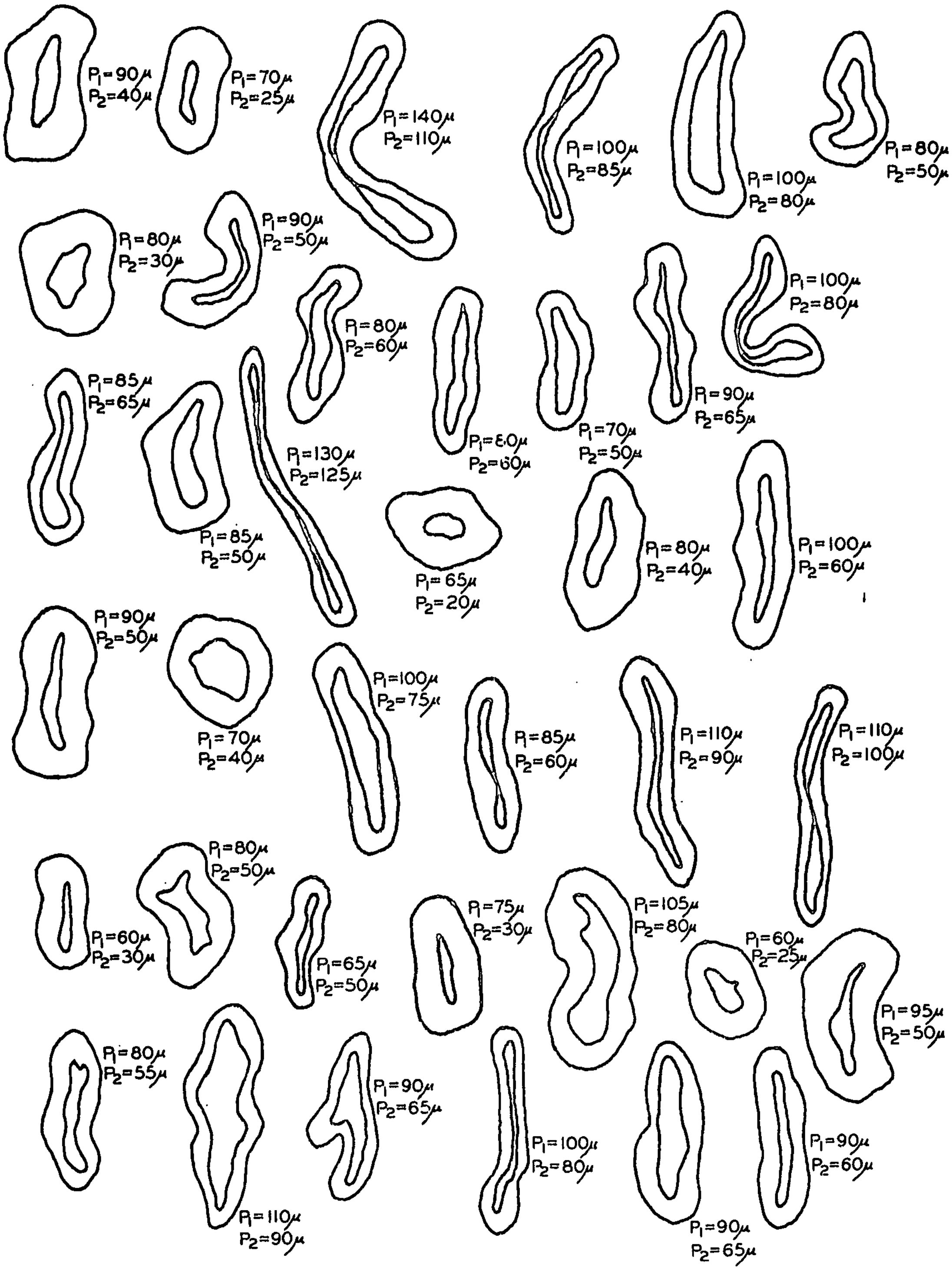


Figure 43 (continued)
Wet Fiber Cross Sections (750X)



P_1 = PERIMETER OF FIBER, MICRONS
P_2 = PERIMETER OF LUMEN, MICRONS

Figure 43 (continued)
Wet Fiber Cross Sections (700X)

C. CALCULATIONS

1. RITTINGER NUMBERS

The difference in power required to run the ball mill with and without the pulps was 13 watts for a 180-gram charge.

Basis: 250 min. beating

$250 \times 13/60 = 54.1$ watt hr. total energy input

$54.1 \times 2656 = 143{,}300$ ft.-lb. total energy input

$100 \times 10^4 \times 180 = 1.8 \times 10^8$ sq. cm. total surface created

$1.8 \times 10^8/1.43 \times 10^5 = 1255$ sq. cm./ft.-lb. Rittinger Number

$7.8 \times 10^4 \times 180 = 1.408 \times 10^7$ sq. cm. external surface created

$1.408 \times 10^7/1.43 \times 10^5 = 98.4$ sq. cm./ft.-lb. Rittinger Number

2. CALCULATIONS FROM MICROSCOPIC DATA

Average perimeter = 92 microns

Average fiber length = 2.16 mm.

Number of fibers per gram = 3,720,000

Therefore, fiber specific surface, S, is given by:

$$S = 9.20 \times 10^{-3} \times 2.16 \times 10^{-1} \times 3.72 \times 10^{6} = 7400 \text{ sq. cm./g.}$$

Weight of 165 fibers = 4.20 g. at magnification of 1000X and on paper of basis weight

$$= 5.97 \times 10^{-3} \text{ g./sq. cm.}$$

Therefore, specific volume of fibers, v, is given by:

$$v = \frac{4.20}{165} \times \frac{10^3}{5.97} \times 10^{-6} \times 0.216 \times 3.72 \times 10^{6} = 3.42 \text{ cc./g.}$$

TABLE XII

MICROSCOPIC MEASUREMENTS

Refining time, min.		0	20	50	100	150	200	250
Arithmetic average fiber length, mm.	Classified	2.16	1.88	1.61	1.52	1.44	1.63	1.35
	Unclassified	1.79	1.77	1.40	1.23	1.26	1.36	1.16
Weighted average fiber length, mm.	Classified	2.96	2.71	2.53	2.44	2.42	2.48	2.35
	Unclassified	2.80	2.80	2.52	2.41	2.31	2.35	2.28
Arithmetic average fiber width, mm.	Classified	0.0358 (wet); 0.0323 (dry)						
Weighted average area, mm.^{2}	Classified	0.085						